MASS TRANSFER AND EQUILIBRIUM IN ADSORPTION FROM DILUTE SOLUTION ONTO POROUS SOLIDS

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CHAPTER 1

INTRODUCTION

1.1 Introductory remarks

Adsorption in liquid phase has been extensively applied to industrial processes. Its field of application does not limit itself into water treatments. Rather, the technique is being utilized as a powerful separation principle in more and more cases. It is partly due to recent advance in production technology for porous material, which has been yielding various types of porous solids, e.g., those with controlled pore characteristics and/or with well-specified surfaces. The importance of liquid phase adsorption should undoubtedly grow further in the future.

The indispensable information for the design of adsorption operation must include mass transport properties and equilibrium characteristics of the system. Both of the two are, however, still left unorganized disciplines at present. The design of an adsorption process must rely, in a greater part, on experience and experiments. The incompleteness confesses that not many research activities have broken apparent phenomena down into basic mechanisms. Sufficient amount of information on the basic mechanisms would enable us to build up well-organized discipline, with which a design of a system could be made efficiently without much experience or, hopefully, even without any experiments.

This dissertation deals with adsorption from dilute solution mainly in two aspects; one of which is of intraparticle mass transfer and the other of

equilibrium. Most of the effort has been paid to pursue the basic mechanisms of the mass transfer and of the equilibrium, and their limit of applicability. The author wishes that these findings would add some contribution to the compilation of basic information for liquid phase adsorption, through which an establishment of the organized discipline in this field should be aimed at.

1.2 Literature review and problems

Intraparticle mass transfer

Transient processes of liquid phase adsorption are often strongly affected by intraparticle diffusion since the intrinsic rate of adsorption at the adsorptive surface in the inside is rapid compared with that of diffusion.

The mass transfer in adsorption or ion exchange process has long been believed to follow the Fickian diffusion. However, a diffusion within the pore volume of the adsorptive porous materials alone could not explain the overall mass transfer rate and had been pointed out that another diffusion mechanism existed within such materials, which was sometimes called "solid-phase diffusion" and is now more commonly termed as "surface diffusion".

In early days of 1950's, the rate process in adsorption was assumed to follow so-called driving-force models for simplification. Among them, two models should be pointed out here. Glückauf and Coates (1947) introduced the linear driving-force model (LDF) which employed the difference between amount adsorbed at particle surface and that averaged over the particle as the driving force of the mass transfer. The other was proposed by Vermeulen (1953) as the quadratic driving force model (QDF), which had quadratic

terms in its driving factor. The latter had been a better approximation for the Fickian diffusion model, especially in initial portion of transient process. The former, however, are still often utilized for the calculation of column adsorption because of its simplicity and of reasonable performance if so-called the constant pattern holds.

More precise treatment on the transient process had been aimed at in the age of 1960's to 70's. The increasing CPU power enabled one to calculate effluent behavior even with the diffusion equation within adsorbent particles. Calculations with Langmuir or Freundlich isotherms were made by Carter (1966), Kyte (1973), Garg and Ruthven (1975), Hashimoto *et al.* (1977) and others. An excellent review in this subject was given by Miura (1980). Through these works, diffusivities came up on discussion instead of the mass transfer coefficients of the driving-force models.

Besides the column adsorption, the mass transport within porous media grew its importance in many aspects such as batch adsorption, membrane separation and catalysis. Thus much work had been made on the diffusivity within porous media in those decades and it was often pointed out that the diffusivity of adsorbed molecules, or surface diffusivity varied with the loading in many cases. In other words the surface diffusivity often has concentration dependency, similarly to the phenomena in gas-phase adsorption. This dependency makes it complicated to treat the rate process in adsorption. However, the dependency itself should be a key to finding the fundamental mechanism of the surface diffusion phenomenon.

From late 70's to 80's, several research works were published on the concentration dependence of the intraparticle diffusivities (Neretnieks, 1976; Sudo *et al.*, 1978; Muraki *et al.*, 1982; Suzuki and Fujii, 1982; Watanabe and Hasatani, 1982; Moon and Lee, 1983; Friedrich *et al.*, 1988; Palosaari *et al.*,

1988; Seidel and Carl, 1988). Among them, the mechanisms of surface diffusion were mentioned in the following articles.

Sudo *et al.* (1978) measured surface diffusivities on virgin adsorbents with various final loadings of batch kinetic experiments. The diffusivities could not stay constant but varied with the loadings. This relation was not strictly a concentration dependence, as they mentioned. Variation of the activation energy with the heat of adsorption was thought to be the cause of the concentration dependence, which was proposed by Gilliland *et al.* (1974) for gas phase on the basis of a model accounting for the hopping of adsorbed molecules. Similar experiments were performed by other researchers (Itaya *et al.*, 1987; Moon and Lee, 1983). However, a concentration dependency in its strict meaning was not measured in these cases.

The concentration dependency in its strict meaning was measured by Suzuki and Fujii (1982) by using a diffusion cell for a steady-state experiment. The measured diffusivity was studied on the same basis as did Gilliland *et al.* (1974) for gas phase, but physical picture was not made clear. An image of the *hopping* of adsorbed molecule *in liquid phase* seems hard to be built up and the determined energy for the hopping was too large compared with that for gas phase. Larger activation energies than those expected from the assumed similarity to the gas-phase surface diffusion were also reported by Komiyama and Smith (1974) and Itaya *et al.* (1987) though the former authors did not show it explicitly.

These results suggest that straightforward application of the treatment of Gilliland *et al.* (1974) may not fully explain the surface diffusion in liquid phase. Besides the concentration dependence, Suzuki and Kawazoe (1975) suggested that the surface diffusivity of various adsorbates on an activated carbon could be correlated with the heat of *evaporation* of the adsorbates.

This contribution of the evaporative energy to the surface diffusion in liquid phase could not be explained in connection with heat of adsorption and has not been interpreted theoretically.

Adsorption equilibrium in liquid phase

Here the subject eliminates adsorption from solution with relatively high concentration in which the surface excess differs significantly from the absolute adsorption amount. An excellent review including this subject was given by Kipling (1965).

In the industrial application, adsorption from dilute solution is of much importance. If concentration of a component to be separated is high, other separation technique would be effective. Adsorption separation could take up dilute components into concentrated state and, at the same time, could purify the solution with small amount of impurity.

Adsorption from dilute solution in liquid phase has often been expressed by an empirical equation, the Freundlich equation. The philosophy has been to express the experimental data by an equation for the sake of convenience. Thus the fundamental mechanism of adsorption from dilute solution has not often been mentioned in literature. Majority of published works dealt with the adsorption of dilute organic solutes from aqueous solutions. This subject is mainly reviewed in the followings.

The first, and still now very much important, approach to the understanding of the phenomena was given by the early work of Polanyi (1920), who had proposed the potential theory of adsorption for gas phase and suggested its applicability to liquid-phase adsorption of solutes with limited solubility. The

experimental verification and improvement of the theory had been made in many works, e.g., Hansen and Fackler (1953) and a long series of research by Manes and co-workers, starting from Manes and Hofer (1969). In the series of Manes, the adsorption of organics with limited solubility from aqueous solution onto activated carbon was proved to follow the theory by the work of Wohleber and Manes (1971). Urano *et al.* (1981) also interpreted isotherms of 16 organic compounds from aqueous solution onto five activated carbons on the basis of the potential theory.

The adsorption potential theory has an extraordinarily long life. It is perhaps because the theory does never assume 'configuration' of adsorption such as the surface geometry, monolayer adsorption and multilayer one, nor does it give any isotherm equation. It simply gives the adsorption volume corresponding to a given potential energy. This kind of essential information expressed by a function, not by a physical *value*, should be of much importance especially in the field with variety of applications. The methodology to elucidate this kind of essential functions should be brushed up in the field of adsorption.

The other significance of the finding of the applicability of the adsorption potential theory to liquid-phase adsorption would be that the similarity between gas-phase and liquid-phase adsorption holds in adsorption onto porous solids. Similarity between them in another aspect was also shown by Hansen *et al.* (1949). They found multilayer adsorption of organics from aqueous solution onto carbons and correlated the amount adsorbed by B.E.T. equations by Brunauer *et al.* (1938), which is well known to describe gas-phase adsorption. Extending these similarities to the higher concentration range, the author has gotten an idea that a similar phenomenon to the so-called capillary condensation of gas-phase adsorption should be possible in liquid-phase adsorption of solutes with limited solubility.

The similar situation in liquid phase to the capillary condensation of gas phase may be as follows; a hindered liquid-liquid equilibrium could stand within a pore because of the presence of a curved interface of the two liquid phases. In other words, a solute-rich phase could be equilibrium with a solvent-rich phase at a lower concentration than the saturated. If this holds in liquid-phase adsorption, pore characteristics of adsorbents should affect the amount adsorbed significantly in higher relative concentrations. Note that the *higher* relative concentration may still be a dilute one if the solubility is not so large. Few research works, however, had pursued the influence of pore characteristics on liquid-phase adsorption (e.g., Stuart, 1958), or mentioned about the hindered liquid-liquid equilibrium within narrow pores. Further, many prominent books on adsorption such as Keii (1965), Defay *et al.* (1966), Gregg and Sing (1967), Ruthven (1984) and Kondo *et al.* (1991) did not mention this phenomenon.

Later the author found that Patrick and co-workers (Patrick and Jones, 1925; Patrick and Eberman, 1925) suggested the possibility of the occurrence of this phenomenon and intuitively proposed a Kelvin-type equation for the relation between pore radius and concentration. However, no sound basis for derivation of the equation nor quantitative tests with experimental data was presented. In spite of its importance expected not only in the field of adsorption but also in many relevant fields, no significant advance seems to have been made since then. In other words this important phenomenon seems to have been *forgotten* for long. Thus the effect of pore sizes on adsorption in liquid phase is still in obscurity and hence almost no guideline has been established for desirable nature of the pore structure of an adsorbent in liquid phase adsorption. The fact that there does not exist a technical term for the phenomenon emphasizes this situation. The author has named it "Capillary Phase-Separation".

1.3 Objectives of this work

The purpose of this dissertation is to give some answers for the understanding of the phenomena of mass transfer and equilibrium in adsorption from dilute solution onto porous solids. The approach has been intended to take up essential information experimentally and to analyze theoretically on as broad a basis as possible, in order to find rules with broader applicability and make their limits clear.

The major obstacle for the understanding of the intraparticle diffusion comes from the lack in experimental data on the concentration dependence. The non-constancy has much been proved in experiments with varied *final* loadings but few works showed the exact relation. Thus first the experimental determination of concentration dependency in its exact meaning has been aimed at. Chapter 2 describes this subject along with a phenomenological correlation of the data obtained.

In Chapter 3, the basic mechanism of surface diffusion phenomenon is discussed on the basis of Eyring's rate theory, which is considered applicable to this phenomenon through the analysis of the equilibrium characteristics based on the potential theory of adsorption. The discussion yields a correlation equation for the concentration/temperature dependency of surface diffusivity with two parameters. The parameters have to be determined through fitting but the validity can easily be judged by their physical meanings defined clearly. The correlation equation is proved to be a general form which includes some correlation equations proposed so far as special cases.

As for the equilibrium, the phenomenon of Capillary Phase-Separation (CPS) is pursued in Chapter 4. A thermodynamic analysis of liquid-liquid equilibrium with curved interface manifests the possibility of solubility reduction, which is named capillary phase-separation — a capillary condensation in liquid phase — As similarly to capillary condensation, the CPS is supposed to have much contribution to the so-called mesoporous solids, whose pore radius ranges mainly from a few to some tens of nanometers. Because of the *forgotten* situation of this phenomenon, no reports seem to have been made about adsorption equilibria on such solids in higher relative concentration. Thus isotherms are measured with variety of combination of solutes and mesoporous solids. The contribution of the CPS is proved to be indispensable for the interpretation of the isotherms. At the same time, the understanding of isotherms on the basis of the CPS phenomenon is utilized as a method for isotherm estimation from pore characteristics of solids.

Chapter 5 deals with a reversed way of utilization of CPS concept. Namely, the understanding of isotherms gives us a way to elucidate pore characteristics of solids in immersed state from liquid-phase adsorption isotherms. One can easily get information on pore characteristics by gas-phase adsorption of, e.g., nitrogen of *evacuated* and *dried* state. However, how can we know the pore characteristics of solids which swell or shrink when immersed in solvent? Some special techniques such as thermoporometry, neutron or X-ray scattering and NMR relaxation could take up topological and morphological information of solids in liquid. However, they need special instruments. Another difficulty with these techniques would be that the theoretical treatment of detected signals are not yet fully established. The utilization of the CPS concept could be an answer to this problem. Thus, the possibility is examined in model cases to show a reasonable performance of porosity detection by liquid-phase adsorption.

Finally, Chapter 6 discusses the whole thesis to give conclusions. The perspectives in these subjects are also discussed.

1.4 Publications on this thesis

Miyahara, M. and M. Okazaki: *J. Chem. Eng. Japan*, **25**, 408 (1992)

Miyahara, M. and M. Okazaki: *J. Chem. Eng. Japan*, **26**, 510 (1993)

Miyahara, M., M. Kato and M. Okazaki: *AIChE J.*, (1994) in press

Miyahara, M. and M. Okazaki: *Fundamentals of Adsorption*, M. Suzuki, ed., p.445, Kodansha, Tokyo (1993)

Miyahara, M. and M. Okazaki: *Chem. Express*, **7**, 601 (1992)

Miyahara, M. and M. Okazaki: *Characterization of Porous Solids III*, J. Rouquerol, ed., Elsevier, New York, (1994) in press

CHAPTER 2

MEASUREMENT OF CONCENTRATION-DEPENDENT SURFACE DIFFUSIVITY AND PHENOMENOLOGICAL CORRELATION

2.1 Introduction

Adsorption processes in liquid phase, such as purification of wastewaters and concentration of dilute components in solutions, are often strongly affected by intraparticle diffusion since the intrinsic rate of adsorption at the adsorptive surface in the inside is rapid compared with that of diffusion. An understanding of the mechanism of intraparticle diffusion is hence necessary for the design of adsorption systems in liquid phase.

It has been pointed out that there exist two modes of mass transfer in porous adsorptive materials. One is the molecular diffusion mode within the pore volume and the other is the so-called surface diffusion mode, which is attributed to the migration of adsorbed molecules on the interior surface of the adsorbent. An important feature of the latter is that the surface diffusivity, D_S, which is naturally defined as a coefficient of mass flux driven by the gradient of amount adsorbed,is concentration dependent (Miura *et al.*, 1975; Sudo *et al.*, 1978; Suzuki and Fujii, 1982; Muraki *et al.*, 1982; Watanabe and Hasatani, 1982, 1984; Moon and Lee, 1983).

Since the surface diffusion often makes a large contribution to the intraparticle mass transfer, the concentration dependency makes it complicated to treat the rate process in liquid-phase adsorption. However,

the dependency itself could be a key to finding the basic mechanism of the surface diffusion phenomenon. Although many previous researches have shown cases in which the surface diffusivity cannot be constant, the surface diffusivities obtained were so-called effective ones; namely, they were not local values with respect to the amount adsorbed. Only a few research results provide locally determined surface diffusivities vs. amount adsorbed (Miura *et al.*, 1975; Suzuki and Fujii, 1982). The mechanism still remains unclear.

In this study, batch adsorption experiments were performed using adsorbents which had been equilibrated with certain liquid concentrations in advance, to obtain local values of surface diffusivity vs. concentration. The concentration dependence obtained was analyzed from the viewpoint of the thermodynamic non-ideality of the amount adsorbed.

2.2 Basic equations

Suppose a stepwise small increase in liquid concentration is given to a batch system of adsorbent and liquid in an equilibrium condition of point A in Figure 2.1. The system starts to change from point B towards a new equilibrium state of point C. The rate constant of this process is, then, a representative one for this concentration interval and hence can be a local value if the interval is small.

Considering both pore and surface diffusion for intraparticle mass transfer, the basic equation for a spherical adsorbent is:

$$\varepsilon\frac{\partial C}{\partial t} + \rho_{app}\frac{\partial q}{\partial t} = D_p\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial C}{\partial r}) + \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\rho_{app}D_s\frac{\partial q}{\partial r}) \qquad (2.1)$$

The following assumptions are made to simplify the equation:

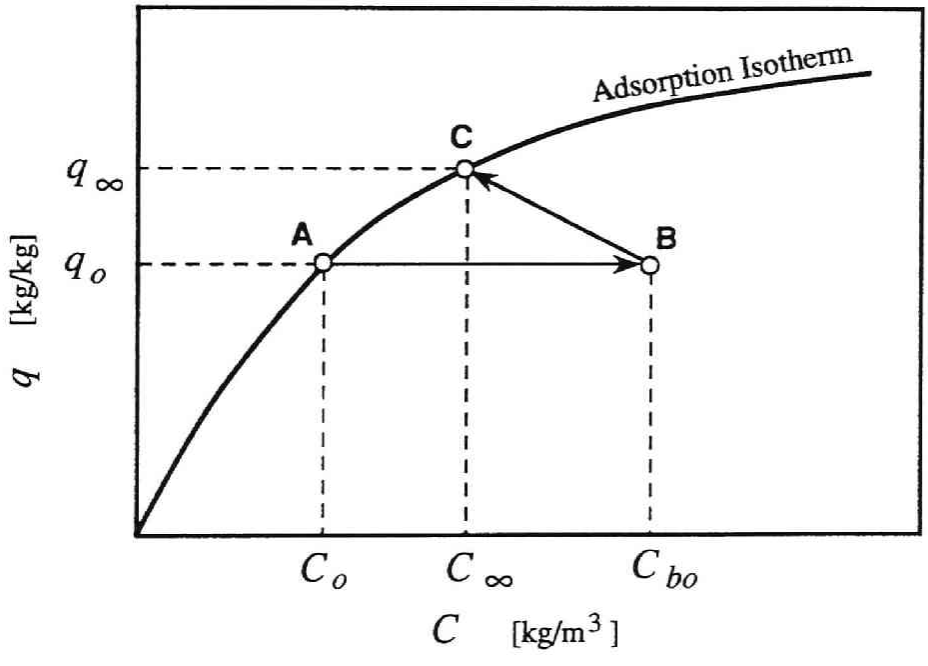

Figure 2.1. Schematic figure of experimental process

1)The local equilibrium condition holds: $q = q(C)$

2)The surface diffusivity D_S and the slope of adsorption isotherm K are approximately constant for the concentration interval considered.

The first assumption is appropriate when the rate of intrinsic adsorption is rapid compared with that of diffusion, as is usually the case with physical adsorption. With the aid of the latter assumption the amount adsorbed, q, can be related to the liquid concentration, C, by a linear relation within the concentration interval. Equation (2.1) then becomes

$$\frac{\partial C}{\partial t} = D_e \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) \tag{2.2}$$

where

$$D_e = \frac{(D_p + \rho_{app} K D_s)}{(\varepsilon + \rho_{app} K)} \tag{2.3}$$

Initial and boundary conditions for Eq.(2.2) are,

$$C = C_o \quad \text{at} \quad t = 0 \tag{2.4}$$

$$C = \text{finite} \quad \text{at} \quad r = 0 \tag{2.5}$$

$$(\varepsilon + \rho_{app} K) D_e \frac{\partial C}{\partial r} = k (C_b(t) - C) \quad \text{at} \quad r = R_p \tag{2.6}$$

For the bulk liquid phase,

$$V_b \frac{dC_b}{dt} = -A_p (\varepsilon + \rho_{app} K) D_e \left[\frac{\partial C}{\partial r} \right]_{r = R_p} \tag{2.7}$$

$$C_b = C_{bo} \quad \text{at} \quad t = 0 \tag{2.8}$$

Equations (2.2) and (2.7) with the above initial and boundary conditions are basically the same as those in Huang and Li (1973) and can be solved by the method of Laplace transformation using the Heaviside expansion formula. The concentration of the bulk liquid is derived to be

$$\frac{C_b - C_o}{C_{bo} - C_o} = \frac{\alpha}{\alpha + 1} + 6\alpha \sum_{n=1}^{\infty} \frac{\exp(-g_n^2 \tau)}{\left[9(\alpha+1) + \alpha^2 g_n^2\right] \quad \alpha(\alpha+6) g_n^2 \frac{1}{Bi} + \alpha^2 g_n^4 \frac{1}{Bi^2}} \tag{2.9}$$

where g_n's are the positive roots of

$$\tan g_n = \frac{g_n (3Bi - \alpha g_n^2)}{3Bi + (Bi \quad 1)\alpha g_n^2} \tag{2.10}$$

and

$$\tau = \frac{D_e t}{R_p{}^2} \tag{2.11}$$

$$\alpha = \frac{3 V_p}{A_p R_p (\varepsilon + \rho_{app} K)} \tag{2.12}$$

$$Bi = \frac{k R_p}{(\varepsilon + \rho_{app} K) D_e} \tag{2.13}$$

In the above Equations, Bi represents the relative importance of the intraparticle mass transfer resistance to the film resistance. A large value of Bi means a small contribution of the film resistance. At the extreme of $Bi \rightarrow \infty$, therefore, the rate is controlled only by the intraparticle diffusion.

The effective diffusivity D_e , together with Bi , can be obtained by fitting Eq.(2.9) to the measured concentration-time curve.

Since D_e consists of the contributions of both surface diffusivity D_S and pore diffusivity D_p , one has to know the latter in advance to obtain D_S from D_e . Since pore diffusivity is related to molecular diffusivity D_{ab} by the parallel pore model as shown in Eq.(2.14), the structural parameter (ε / μ) of the adsorbent must be determined.

Table 2.1 Properties of the adsorbent

Shape		Spherical
Diameter	[m]	1.30×10^{-3}
Apparent density	[kg/m^3]	690
Total porosity	[-]	0.65
Macro porosity	[-]	0.31
Micro porosity	[-]	0.34
Nitrogen surface area	[m^2/kg]	7.2×10^5

$$D_p = \left[\frac{\varepsilon}{\mu}\right] D_{ab} \tag{2.14}$$

where μ represents the tortuosity of the adsorbent. To exclude the influence of surface diffusion, a non-adsorptive or relatively non-adsorptive compound should be used as a diffusing species in the kinetic experiments to obtain tortuosity. Details are described in the following sections.

2.3 Experimental

The adsorbent used was a commercial activated carbon, Takeda X-7000, whose shape was spherical. The physical properties are listed in Table 2.1. All adsorbent particles were washed with distilled water and evacuated at 383K for 24 hours before experimental use. Nitrobenzene and benzonitrile of research grade provided by Wako Pure Chemicals Inc. were used as adsorbate without further purification.

The isotherms were determined by the conventional method: the adsorbent was added to 300 ml solution in an Erlenmeyer flask stopped by a Teflon-sealed screw cap, and shaken in a thermostatted bath at 308K. The

equilibrium concentrations of nitrobenzene and benzonitrile were determined by an ultraviolet spectrophotometer (Shimadzu UV-260) at the wavelengths of 267 and 224nm, respectively.

A schematic sketch of the adsorber is shown in Figure 2.2. A stirred tank (124mm I.D.) made of Pyrex glass was equipped with two baffles (80x28x8mm) made of 60 mesh stainless wire screen, which can hold the adsorbent inside. A six-bladed impeller (50x10mm) made of stainless steel was rotated at about 1000 r.p.m. during the kinetic experiment.

A small amount of sieved adsorbent (14/16 mesh) was brought into contact with a solution to yield an equilibrium condition of C_O and q_O, which is also a starting point in the kinetic experiment. The adsorbent baskets were lifted up temporarily from the solution and the liquid concentration was raised to C_{bo}. As a standard condition, C_{bo}/C_O was equal to about 1.5 while in the higher concentration range a ratio of 1.7 was needed to yield a reliable concentration-time relation. These ratios were still logarithmically small enough, compared with the whole concentration range investigated, to give local diffusivities. At t =0 in the kinetic experiment, the adsorbent basket was suddenly immersed in the agitated solution. A stepwise increase in liquid concentration was achieved by this procedure. Measurements were made by taking small samples from the solution at pre-determined intervals and monitoring the concentration with a spectrophotometer.

For the determination of the pore diffusivity D_p, glucose, the amount adsorbed of which was confirmed to be negligibly small compared with nitrobenzene and benzonitrile, was used as a diffusing species. The kinetic experiments in this system were performed by almost the same procedure as that for the surface diffusion measurement except that the bulk initial concentration was zero; that is, desorption runs were adopted in this system.

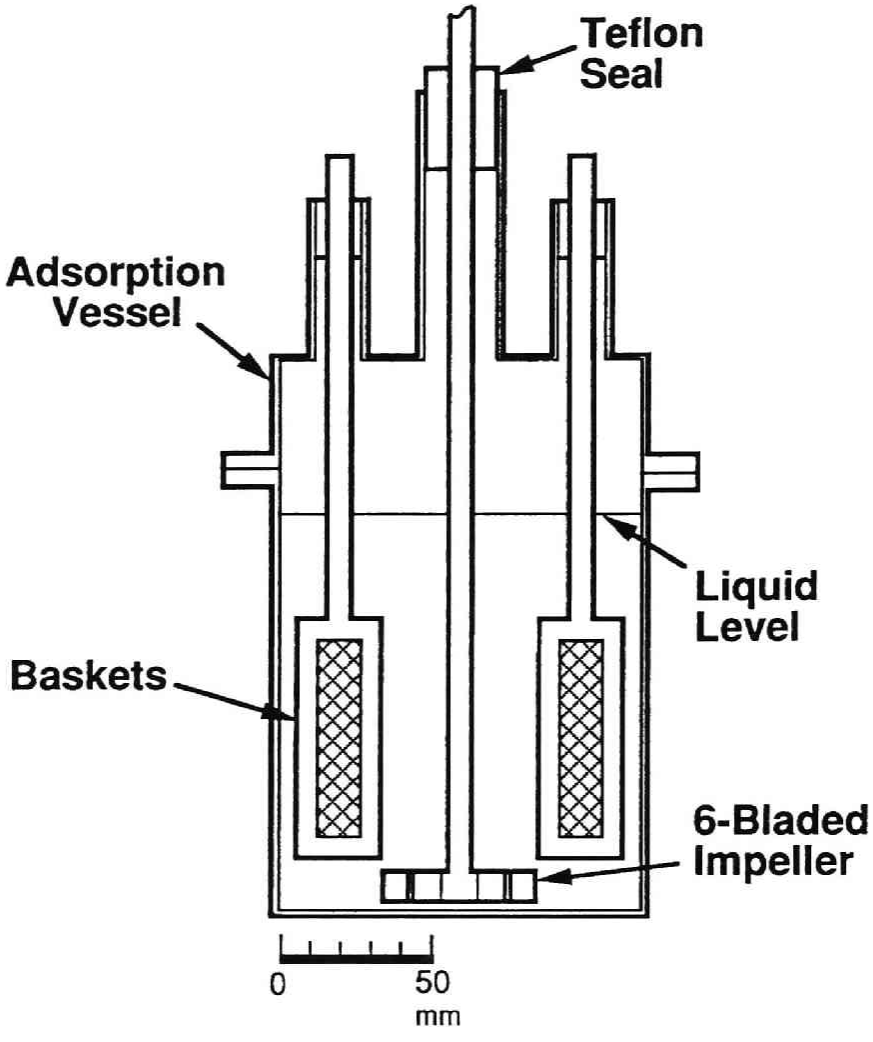

Figure 2.2. Schematic sketch of the adsorber

Concentrations were measured by a total organic carbon analyzer (Shimadzu TOC-10A).

2.4 Results and discussion

2.4.1 Isotherms

The isotherms of nitrobenzene and benzonitrile measured at 308K are shown in Figure 2.3. Though both isotherms have straight portions, an incipient shift to Henry's law in the lower concentration range for nitrobenzene and asymptotic behavior to saturation in the higher concentration range for both adsorbates are recognized. As a result, the Freundlich equation can only partly express the isotherms of the systems studied.

2.4.2 Effective diffusivity

Some results of the kinetic experiments are illustrated in Figure 2.4 together with the curves fitted by Eq. (2.9). The curves agree fairly well with the experimental points. The agreements were similar in all the experiments, which confirmed the validity of the assumptions adopted in this study. The effective diffusivity thus obtained increased significantly with concentration.

It should be noted that the Biot numbers fall into finite values rather than infinity. This means that the external mass transfer resistance cannot be neglected in this system, even under such an intensive mixing condition as mentioned above. A considerable increase in the intraparticle mass transfer rate by surface diffusion is thus expected in this system. The external mass transfer coefficients were calculated by Eq.(2.13) to be around 2×10^{-4} m/s, which was roughly equivalent to the Sherwood number of 200. Similar values have been reported by Muraki *et al.* (1982) where almost the same type of adsorber was used, and also in several studies (Suzuki and Kawazoe,

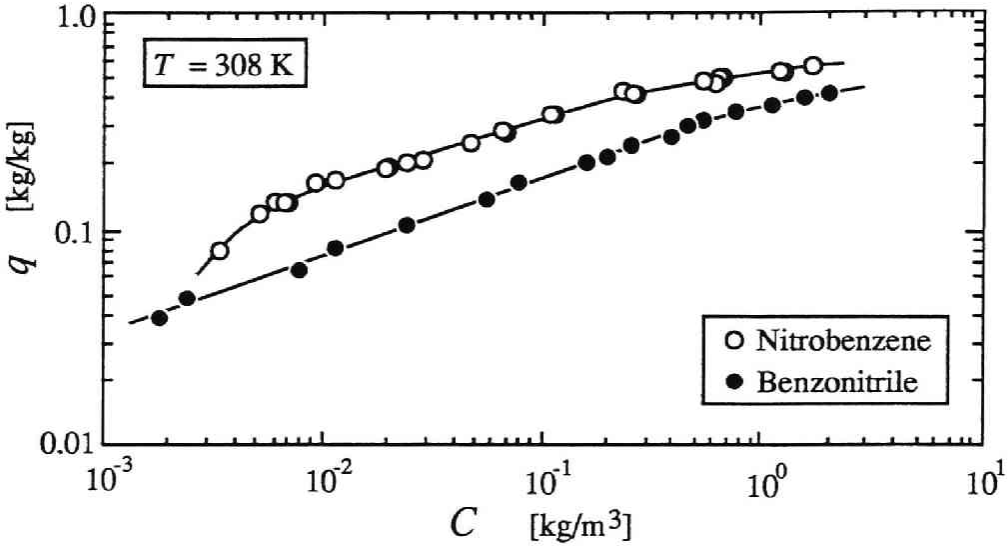

Figure 2.3. Adsorption isotherms of nitrobenzene and benzonitrile

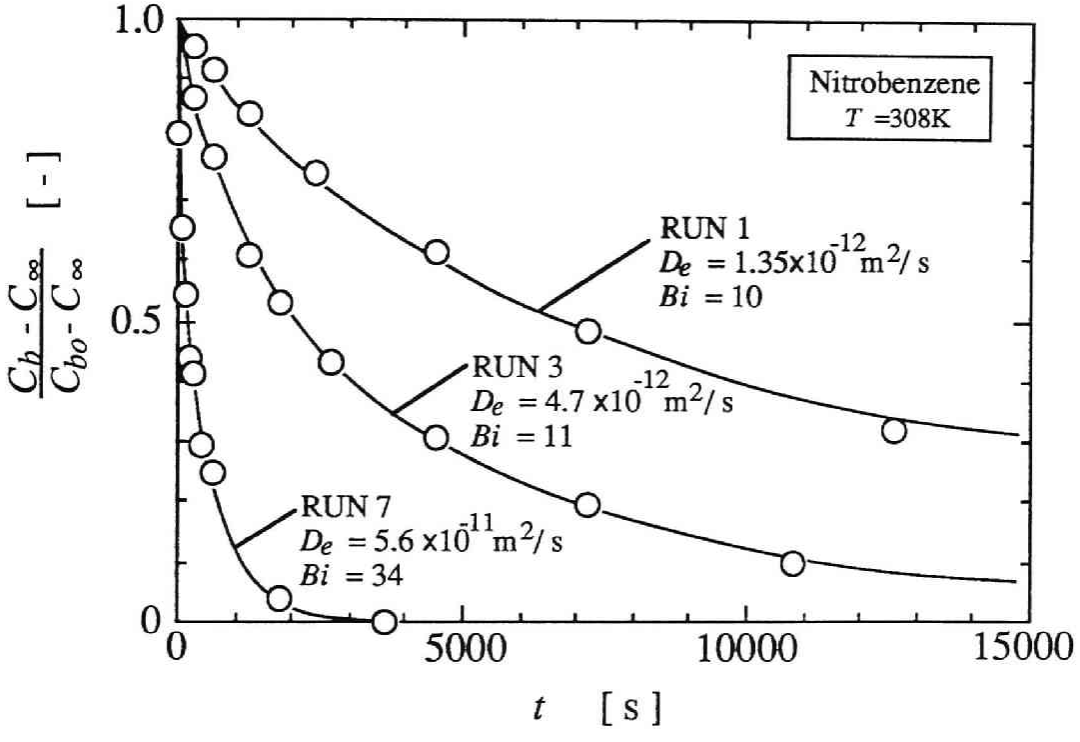

Figure 2.4. Batch kinetic experiments of nitrobenzene

1975; Peel *et al.*, 1981; Moon and Lee, 1983) where adsorbents were held by impellers instead of baffles.

2.4.3 Pore diffusivity

It is often the case that intraparticle mass transfer is controlled by surface diffusion in the physical adsorption in liquid phase. It was confirmed that this was the situation in the system studied. The results are described briefly below.

In some preliminary experiments on the adsorption equilibrium of glucose solution, the amount adsorbed was confirmed to be so small that a negligible contribution of surface diffusion could be assumed. However, the amount itself could not be neglected in comparison with that held in the pore volume. The effective diffusivity for this system is thus expressed as follows:

$$D_e = \frac{D_p}{(\varepsilon + \rho_{app} K)} \tag{2.15}$$

The denominator of the above equation can be determined by a mass balance between the initial and final conditions of the kinetic experiment as done by Komiyama and Smith (1974).

$$\varepsilon + \rho_{app} K = \frac{\rho_{app} V_b}{W_a} \frac{C_\infty}{C_o - C_\infty} \tag{2.16}$$

Figure 2.5 shows the result of a kinetic experiment for glucose. The fitted curve of Eq. (2.9) agrees well with the data. Note that the Biot number must have an infinitely large value to get the best fit here, in contrast to those of the adsorptive compounds. Since the intraparticle mass transfer was controlled only by the pore diffusion, there was no acceleration of mass transfer inside the particle. This lead to the situation in which the film mass transfer outside

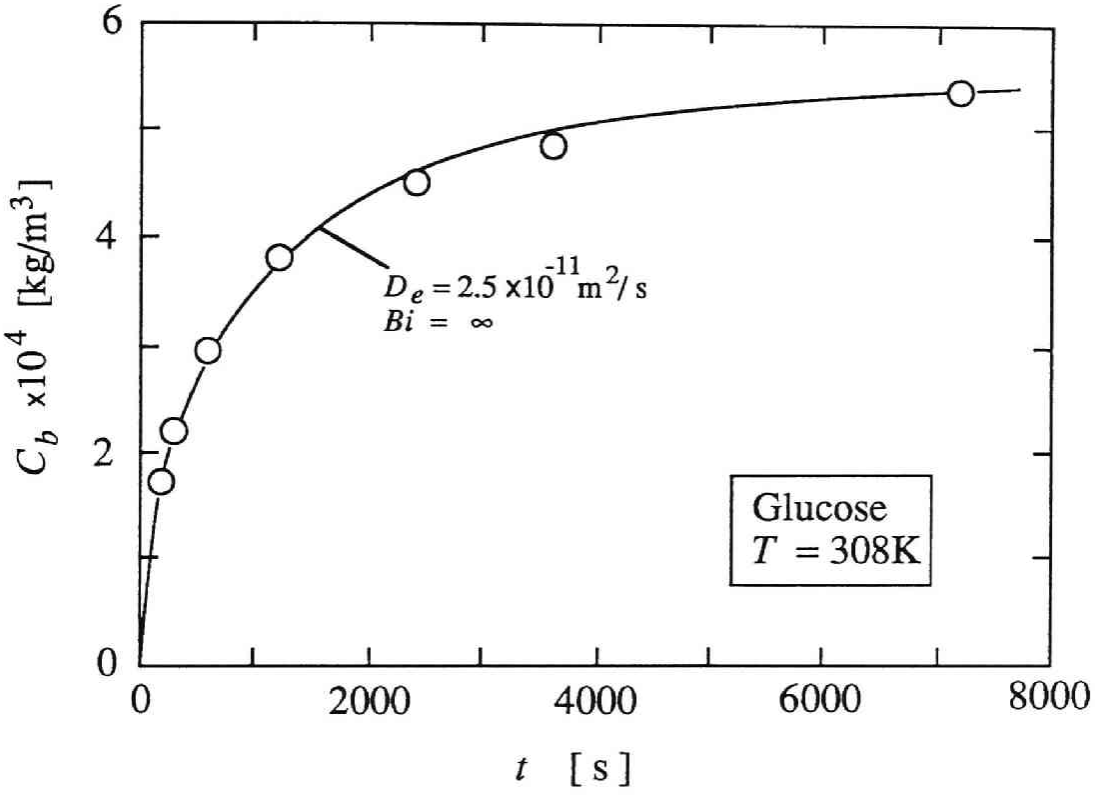

Figure 2.5. Desorption experiment for glucose

the particle was far rapid compared with that in the particle. Thus the Biot number must have an infinitely large value which means negligible film mass transfer resistance.

The structural parameter obtained is as follows:

$(\varepsilon/\mu) = 0.078$

Though the tortuosity itself need not be determined, its calculation was attempted to obtain μ =4.0 using macro-porosity, 0.31, in ε term according to the recommendation by Kawazoe *et al.* (1966). This value is consistent with other research results obtained so far for activated carbons, such as those of Kawazoe *et al.* (1966).

D_p 's for the nitrobenzene system and benzonitrile system were calculated by Eq.(2.14). As shown by Eq.(2.3), the contribution of the pore diffusion can be evaluated with comparison of D_p and $(\varepsilon+\rho_{app}K)D_e$. For example, D_p for nitrobenzene was 1.1×10^{-10} m^2/s at 308 K, while the latter term ranged from 4.4×10^{-9} to 1.6×10^{-8} m^2/s at 308K. It was confirmed that the pore diffusion contributed only a few percent of the total mass flux in all the experiments. Hence, the surface diffusivity can be approximated by the effective diffusivity in the systems of adsorptive compounds studied.

2.4.4 Concentration dependence of surface diffusivity

Surface diffusivities are plotted against the amount adsorbed in Figure 2.6. They vary almost a hundredfold with the amount adsorbed. Such significant concentration dependency as a variation of almost two orders of magnitude is first confirmed by the authors experimentally in liquid-phase adsorption in the present study. They seem empirically to be correlated by an exponential function. However, this type of function has little theoretical basis for the isotherms of the systems studied here. In addition, the data seem to have a sigmoid form rather than to be exponentially linear.

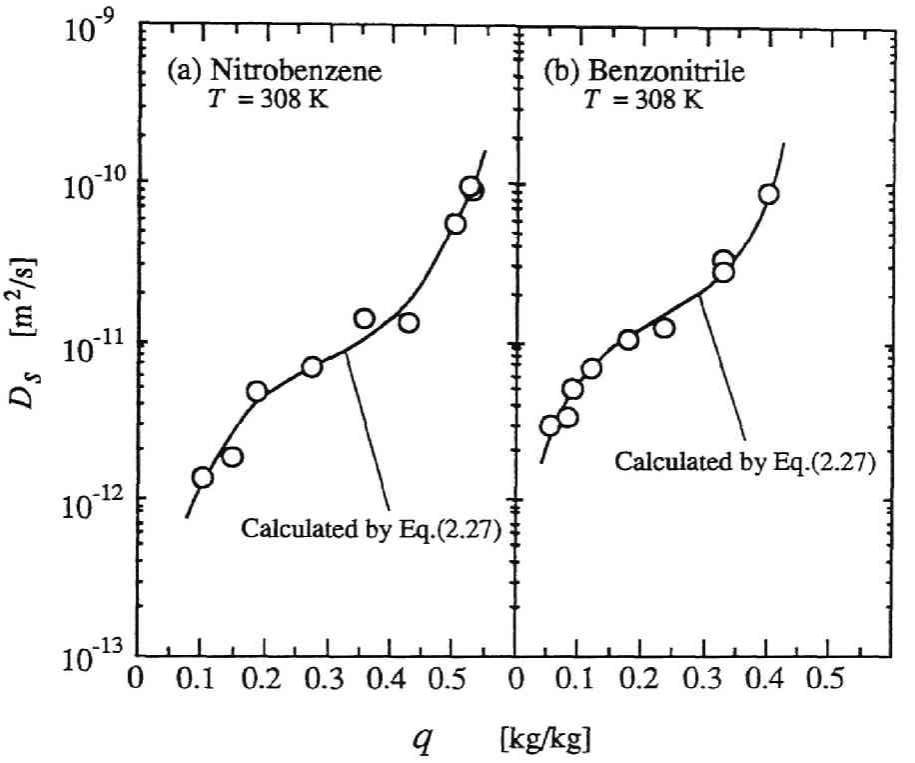

Figure 2.6. Relation between surface diffusivity and amount adsorbed (a) for nitrobenzene and (b) for benzonitrile

A correlation of D_S by a power function formula of q has been proposed for Freundlich isotherms (Suzuki and Fujii, 1982; Muraki *et al.*, 1982), based on a similar concept proposed by Gilliland *et al.* (1974) for gaseous phase adsorption; the activation energy of surface diffusion is assumed to vary linearly with the heat of adsorption. This assumption leads to Eq.(2.17).

$$D_s = D_s^* \, (q / q^*)^{(a\,n)} \tag{2.17}$$

This formula might be applicable to the middle concentration range of nitrobenzene and the major part of the concentration range of benzonitrile, where the isotherms were relatively straight, to prove the partial applicability of Freundlich equations. However, the power function is obviously not suitable for the whole range of the dependency obtained here, because the power function should be convex to the abscissa in Figure 2.6 whereas the data show sigmoidal changes.

In ordinary diffusion in liquid phase, concentration dependence of the diffusivity is often caused by the nonlinearity of liquid concentration against activity. The amount adsorbed, q, is thought to be typical of nonlinear factors. The surface diffusivity, which is defined with the nonlinear quantity, must be affected by the nonlinearity. Introducing *mobility of adsorbed molecule* by a similar concept to ordinary liquid-phase diffusion, we can examine the effect of nonlinearity. Similar concept has often been applied for intracrystalline diffusion within, e.g., zeolites. However, no attempts seem to have been made for the surface diffusivity. Thus the mobility for surface diffusion is considered as follows.

Consider adsorbed molecules subjected to a gradient of the amount adsorbed. The chemical potential of adsorbed phase at a point $z = z$ can be expressed by

a liquid-phase activity which can be in equilibrium with the amount adsorbed at z. Accordingly, the force acting on an adsorbed molecule is expressed as

$$\begin{aligned} F &= -\frac{1}{N_A}\cdot\frac{\partial \mu_a}{\partial z} \\ &= -\frac{1}{N_A}\cdot\frac{\partial \mu_{l(C)}}{\partial z} \\ &= -k_B T\frac{\partial \ln a_i}{\partial z} \end{aligned} \tag{2.18}$$

Denoting the mobility of an adsorbed molecule as u_a, the average velocity of adsorbed molecules is

$$v_a = u_a \cdot F \tag{2.19}$$

Since the amount adsorbed per unit volume is the product of ρ_{app} and q, the mass flux of adsorbed molecules is given by

$$\begin{aligned} J_s &= \rho_{app} q v_a \\ &= -\rho_{app} q u_a k_B T\frac{\partial \ln a_i}{\partial z} \end{aligned} \tag{2.20}$$

On the other hand, the definition of the surface diffusivity is

$$J_s = -\rho_{app} D_s \frac{dq}{dz} \tag{2.21}$$

which is compared with Eq.(2.20) to yield

$$D_s = k_B T\, u_a \left(\frac{\partial \ln a_i}{\partial \ln q}\right)_T \tag{2.22}$$

The activity of adsorbate in solution could be substituted by the liquid-phase concentration provided linearity between them holds — for example, under ideal dilute solution approximation which is the case in this study.

$$D_s = k_B T \, u_a \left(\frac{\partial \ln C}{\partial \ln q} \right)_T \tag{2.23}$$

The term in the parenthesis means the reciprocal exponent of the adsorption isotherm. If the Freundlich isotherm holds in a given system, the term stays constant. The mobility is then simply in proportion to the surface diffusivity at a given temperature. Thus we do not have much benefit to introduce the mobility in discussing the concentration dependence provided that the Freundlich isotherm holds. For other isotherms, however, the apparent variation of D_S can be separated into that caused by the nonlinearity effect and that by other effect. u_a 's represent the variation which do not include the nonlinearity effect. Thus the introduction of u_a enables us to discuss the mass transfer rate more precisely.

The D_S data can be converted to u_a data with the aid of the information from isotherms, namely the logarithmic slopes of the adsorption isotherms which are shown in Figures 2.7 and 2.8. In the middle concentration range of nitrobenzene and in the major concentration range of benzonitrile, the slope shows almost constant value, which corresponds to the straight portion in Figure 2.3. In the higher concentration range both systems show decreasing slopes. Not so many adsorption data exist for 308 K. However, the logarithmic slopes of the isotherms are determined using all the data including those at other temperatures as will be shown in the next chapter. If an isotherm reaches to saturation and has nearly a flat part, the slope would have quite a big uncertainty. Fortunately, however, the slopes could be determined with reasonable accuracy in the systems studied here.

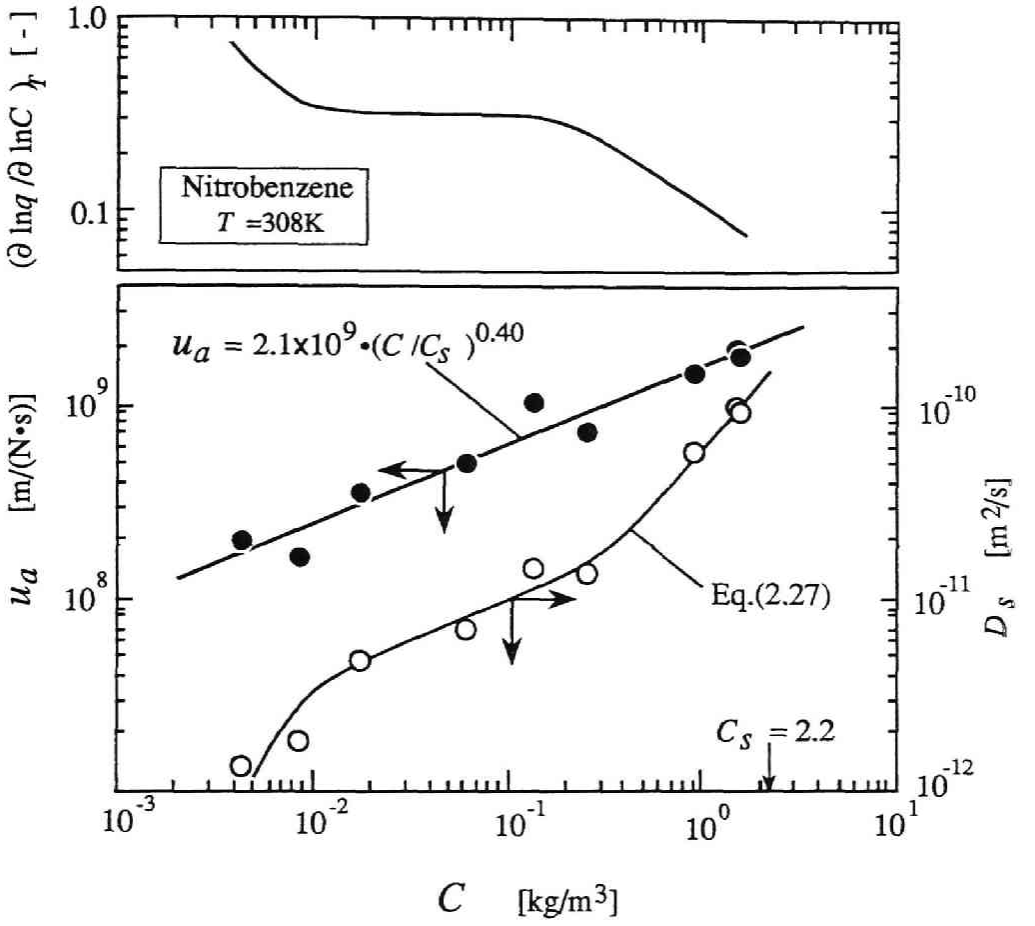

Figure 2.7. Correlation of mobility and surface diffusivity with liquid concentration for nitrobenzene

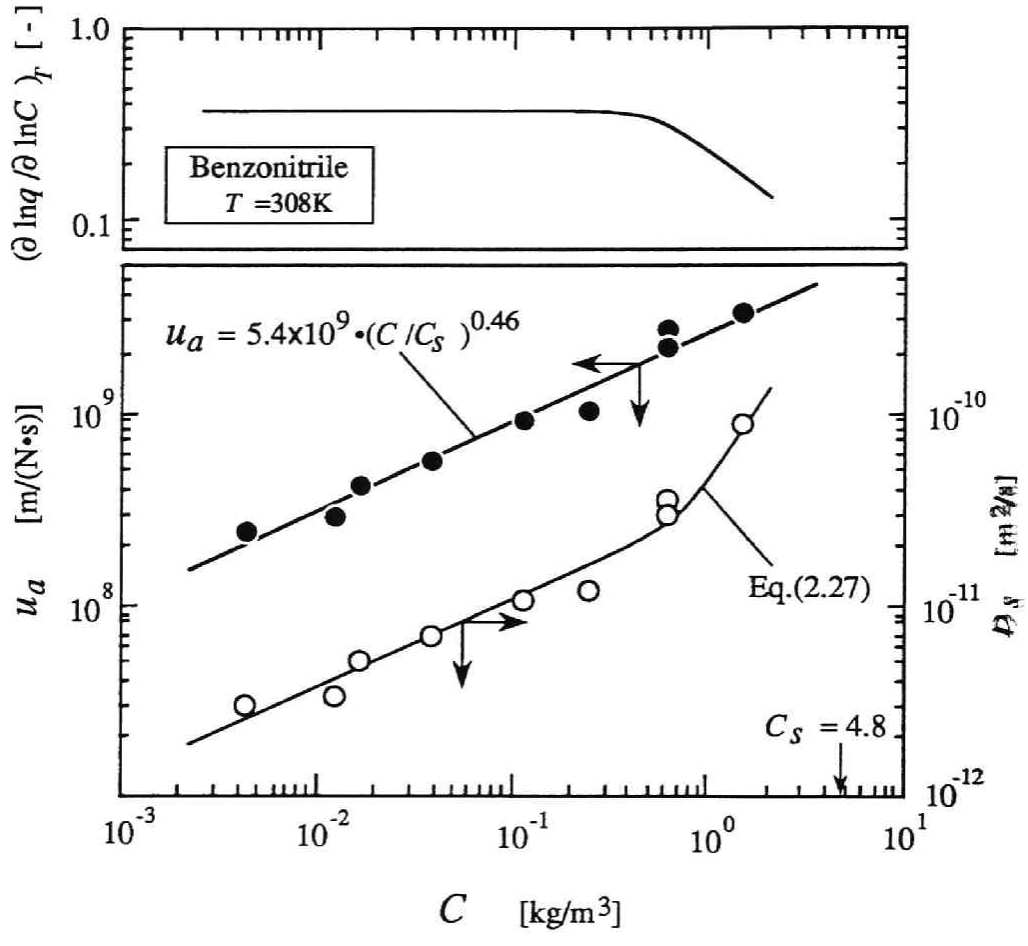

Figure 2.8. Correlation of mobility and surface diffusivity with liquid concentration for benzonitrile

The obtained u_a's are plotted against C also in Figures 2.7 and 2.8 together with the D_S data for reference. For each system, the u_a's seem to be correlated by a straight line with slope of 0.4–0.5 as expressed by the correlation equations in the figures. Though we have to admit relatively large uncertainty in the logarithmic slope of the isotherm, the linearity obtained is quite promising.

This linearity could be interpreted as follows. Let us assume an Arrhenius-type of expression for the mass transfer property u_a .

$$u_a = k_o \exp(- \frac{\Delta E_a}{RT}) \tag{2.24}$$

It is acceptable to set a linear relation between the activation energy and adsorptive energy as done by Gilliland *et al.* (1974), Suzuki and Fujii (1982) and Muraki *et al.* (1982). For adsorbate with small solubility, the isosteric heat of adsorption may be approximated by the sum of the adsorption potential and the heat of dissolution as derived by Urano *et al.* (1981). Though they showed this relation only for the Freundlich isotherm, the relation should be true for any type of isotherm as long as we accept the theory of adsorption on heterogeneous surfaces proposed by Roginsky (1949) and take the saturation concentration, C_S , for the standard concentration of energy term as explained by Seidel and Carl (1989).

$$q_{st} = RT \ \ln(C_s / C \ ) + \Delta H_{sol} \tag{2.25}$$

A linear, not necessarily proportional, relation between ΔE_a and q_{st} is sufficient to yield the power function formula at a certain temperature.

$$u_a = u_{ao}\left(\frac{C}{C_s}\right)^a \tag{2.26}$$

Combining with Eq.(2.23),

$$D_s = k_B T \, u_{ao} \left(\frac{\partial \ln C}{\partial \ln q} \right) \left(\frac{C}{C_s} \right)^a \tag{2.27}$$

where a is the coefficient of linear expression of ΔE_a with q_{st}. Equation (2.27) is considered to be a general form of Eq.(2.17) since it reduces to Eq.(2.17) if the Freundlich isotherm holds.

Note that the mobility used here is distinguished from the reciprocal of resistance coefficient derived by Gilliland *et al.* (1958). The trial of their correlation was not successful.

Figures 2.7 and 2.8 show that a is around 0.4-0.5 for these aromatic compounds. This result is in line with those obtained by Muraki *et al.* (1982) for three kinds of aromatic compounds with Freundlich isotherms, where the concentration-time curves of kinetic experiments using virgin carbons were analyzed numerically using Eq.(2.17) for surface diffusivity.

Using the correlation equations of the mobilities, Eq.(2.27) gives the calculated surface diffusivity as shown by the solid lines in Figures 2.7 and 2.8. They are also shown against q in Figure 2.6 with the aid of isotherm relations. The calculated curves well correlate the D_S data in the whole range of the concentration investigated. The sigmoid change in Figure 2.6 can now be understood as follows. While the logarithmic slope is constant over a certain range of concentration, Eq.(2.27) reduces to a simple power function of q, as stated above, to yield a convex portion. The decrease in logarithmic slope in the higher concentration range as shown in Figures 2.7 and 2.8 results both in the rise in D_S against C as seen in the figures, and in the quite

small change of q against C as shown by isotherms, thus yielding a steep rise in D_S -q plots in Figure 2.6. As a result, the plot of D_S against q shows a sigmoid form rather than a convex or exponentially linear one.

As explained, the logarithmic linearity between u_a and C could be resulted from the variation of the activation energy which is corresponding to the decrease of adsorptive energy. However, the theoretical basis for the connection of the diffusivity or mobility with temperature remains unclear. Consideration of the basic mechanism of surface diffusion would be desirable to solve this problem.

2.5 Conclusions

Local values of surface diffusivities were determined through batch kinetic experiment in limited ranges of amount adsorbed. Pore diffusion was confirmed to make a negligible contribution to intraparticle mass transfer through kinetic experiments using a relatively non-adsorptive substance as diffusing species, while the film resistance could not be neglected.

Introduction of *mobility of adsorbed molecule* and assumption of change in mobility with energy of adsorption well correlated the surface diffusivity obtained with amount adsorbed in the whole range of concentration investigated.

CHAPTER 3

INTERPRETATION OF CONCENTRATION-DEPENDENT SURFACE DIFFUSIVITY BASED ON EYRING'S RATE THEORY

3.1 Introduction

Though the adsorption technique has been broadening its field of applications, the mass transport mechanisms within the adsorptive material still remain unclear, especially for liquid-phase adsorption. Adsorbed molecules can migrate along the interior surface of adsorptive material to show anomalously large transport rate compared with that expected from the diffusion within the pore volume only. The difficulty lies in this phenomenon, so-called surface diffusion. The intraparticle mass transfer is often dominated by surface diffusion and the surface diffusivity varies with the amount adsorbed in many cases. This dependency makes it complicated to treat the rate process in adsorption. However, the dependency itself could be a key to finding the fundamental mechanism of the surface diffusion phenomenon.

As far as the gas-phase surface diffusion is concerned, many papers on the transport mechanism have been reported (Higashi *et al.*, 1963; Gilliland *et al.*, 1974; Okazaki *et al.*, 1981a, 1981b; Tamon *et al.* 1981). For liquid-phase surface diffusion, however, understanding of the basic mechanism is quite limited at present.

Sudo *et al.* (1978) measured surface diffusivities on virgin adsorbents with various final loadings in batch kinetic experiments. This relation was not strictly a concentration dependence, as they mentioned. Variation of the activation energy with the heat of adsorption was thought to be the cause of the concentration dependence, which was proposed by Gilliland *et al.* (1974) for gas phase on the basis of a model accounting for the hopping of adsorbed molecules. Similar experiments were performed by other researchers (Moon and Lee, 1983; Itaya *et al.*, 1987).

Suzuki and Fujii (1982) measured concentration dependency in its strict meaning by using a Wicke-Kallenbach type of diffusion cell and studied on the same basis as did Gilliland *et al.* (1974). This yielded a power function correlation with Freundlich isotherm. They obtained an activation energy of surface diffusion *equal* to the isosteric heat of adsorption. For gas-phase surface diffusion, the activation energy was smaller than the heat of adsorption; the ratios were mostly around 0.5 (Gilliland *et al.*, 1974; Okazaki *et al.*, 1981a). Larger activation energies than those expected from heat of adsorption were also reported by Itaya *et al.* (1987) and Komiyama and Smith (1974), though the latter authors did not show it explicitly.

These results suggest that straightforward application of the treatment of Gilliland *et al.* (1974) may not fully explain the surface diffusion in liquid phase. Besides the concentration dependence, Suzuki and Kawazoe (1975) suggested that the surface diffusivity of various adsorbates on an activated carbon could be correlated with the heat of evaporation of the adsorbates. This contribution of the evaporative energy to the surface diffusion in liquid phase could not be explained in connection with heat of adsorption and has not been interpreted theoretically.

In the preceding chapter the concentration dependency of surface diffusivity was determined from kinetic experiment data within limited ranges of the amount adsorbed. However, the activation energy itself was not analyzed in detail because of the lack of temperature dependency. In this chapter, a new correlation of the surface diffusivity is proposed to explain both concentration and temperature dependency, which also accounts for the relevance of evaporative energy to the surface diffusion. The correlation is based on Eyring's rate theory. Thus the parameters in the correlation have sound definitions. The correlation is tested with data shown in the preceding chapter and those in this chapter. The accord with other literature data is also discussed.

3.2 Experimental

The adsorbent used was a commercial activated carbon X-7000 provided by Takeda Chemical Industries Ltd., spherical in shape and sieved (14/16 mesh) to uniform size. Nitrobenzene and benzonitrile were used as adsorbates. The isotherms were measured by the conventional batch adsorption method. The concentrations were measured by an ultraviolet spectrophotometer.

Batch kinetic experiments were performed in an adsorber (124mm I.D.) equipped with two baffles made of stainless-steel screen which could hold the adsorbent inside. The adsorbent, which had been pre-loaded — namely, equilibrated with a certain concentration — was used in a kinetic experiment to obtain the adsorption rate representing the corresponding range of amount adsorbed. The range was narrow so that the diffusivity obtained could be considered a local value. Five to nine sets of the kinetic experiments were performed for each adsorbate at each temperature.

The experiments were made at 293K and 323K for nitrobenzene and 293K for benzonitrile. More details were shown in the preceding chapter, in which the experiments were made at 308K for both adsorbates.

3.3 Theory

3.3.1 Definition of surface diffusivity

The surface diffusivity is defined for a sectional area which includes both pore volume and solid.

$$J_s = -\rho_{app} D_s \frac{dq}{dz} \tag{3.1}$$

where J_S is the mass flux due to surface diffusion and z denotes the distance coordinates within an adsorbent particle. Accordingly, D_S includes structural factors such as tortuosity and porosity.

Since pore diffusion sometimes contributes to the intraparticle mass transfer, the total mass flux is expressed as

$$J_t = J_s + J_p = -\rho_{app} D_s \frac{dq}{dz} - D_p \frac{dC}{dz} \tag{3.2}$$

Here, parallel contributions of the two mechanisms are employed since the apparent mass fluxes obtained were far larger than expected from pore diffusion in this adsorbent as shown in Chapter 2. The surface diffusivity should be determined by subtracting the contribution of the pore diffusion from the total mass transfer rate. The tortuosity of the adsorbent was 4.0, as determined from kinetic data with non-adsorptive solute as stated in the preceding chapter. The contribution of the pore diffusion was confirmed to be negligible.

3.3.2 Application of Eyring's rate theory to surface diffusion

The elemental steps of surface diffusion are thought to be

i) generation of a hole beside an adsorbed molecule

ii) movement of the neighboring molecule into the hole, surmounting an energy barrier between the two places

The free energy of the activation of these successive steps is denoted as $\Delta F^{\ddagger}$. Application of Eyring's rate theory to the process yields the rate constant, or the frequency of movement of the adsorbed molecule as

$$k = \frac{k_B T}{h} \exp\left(-\frac{\Delta F^{\ddagger}}{RT}\right) \tag{3.3}$$

Here $\Delta F^{\ddagger}$ can be dependent on the amount adsorbed. At a certain location $z = z$ where $q = q$, the frequency k may have a distribution over the range of the amount adsorbed, $0<q'<q$. The mass flux at a location should be obtained by an integration over this distribution using q' as a variable for the integration. The non-ideality of the intensity factor, q, also should be considered. Thus the mass flux by surface diffusion can be obtained as (See Appendix)

$$J_s = -\rho_{app} \frac{\lambda^2}{\mu_s} \frac{k_B T}{h} \exp\left(-\frac{\Delta F^{\ddagger}}{RT}\right) \left(\frac{\partial \ln a_i}{\partial \ln q}\right)_T \frac{dq}{dz} \tag{3.4}$$

Note that $\Delta F^{\ddagger}$ only at $q' = q$ appears in the equation finally. By comparing Eqs. (3.1) and (3.4), the surface diffusivity is obtained as

$$D_s = \frac{\lambda^2}{\mu_s} \frac{k_B T}{h} \exp\left(-\frac{\Delta F^{\ddagger}}{RT}\right) \left(\frac{\partial \ln a_i}{\partial \ln q}\right)_T \tag{3.5}$$

The solutions studied can be approximated as ideal dilute solution. Since the activity is in proportion to the concentration, Eq. (3.6) holds.

$$D_s = \frac{\lambda^2}{\mu_s}\frac{k_B T}{h}\exp(-\frac{\Delta F^{\ddagger}}{RT})\left(\frac{\partial \ln C}{\partial \ln q}\right)_T \tag{3.6}$$

On the other hand, Eq. (3.7) shows the definition of mobility of adsorbed molecule whose driving force is the gradient of chemical potential.

$$D_s = k_B T\, u_a\left(\frac{\partial \ln C}{\partial \ln q}\right)_T \tag{3.7}$$

Equations (3.6) and (3.7) yield

$$u_a = \frac{\lambda^2}{\mu_s h}\exp(-\frac{\Delta F^{\ddagger}}{RT}) \tag{3.8}$$

The D_S data can be converted by Eq.(3.7) to u_a data with information of isotherms. Since u_a does not include the logarithmic slope of the adsorption isotherm, this transport property is thought to be appropriate for correlation in systems with non-Freundlich type adsorption isotherms.

The variations of λ with the amount adsorbed and with temperature are considered to be negligibly small. The most important factor which is the cause of the change in D_S must be the free energy of activation, $\Delta F^{\ddagger}$. The characteristic of this factor is discussed in the following section.

3.3.3 Free energy of activation

1) Potential theory of adsorption As stated, the activation energy consists of two elemental steps: namely, the hole-making step and the succeeding

Table 3.1 Physical properties of adsorbates

Adsorbate		Nitrobenzene			Benzonitrile	
Temperature		293K	308K	323K	293K	308K
Saturation conc.	[kg/m^3]	1.84	2.2	2.6	4.0	4.8
Liquid density	[kg/m^3]	1200	1190	1170	1000	990
Evaporative energy	[kJ/mol]	52.6	51.8	51.0	55.7	53.4

movement. The equilibrium character of adsorbed molecules is considered to decide which step is dominant.

An early work of Polanyi (1920) and many research results, for example those of Urano *et al.* (1981), have pointed out that the potential theory of adsorption can be applied to the liquid-phase adsorption of solutes with limited solubility. The isotherm data at different temperatures were converted to adsorption potential, $RT \ln(C_S/C)$, and adsorption volume W. The physical properties used are listed in Table 3.1. The results are shown in Figure 3.1. As seen, the data at different temperatures can be expressed by a single characteristic curve. The potential theory can explain the equilibrium states of the system.

The potential theory has the basis that the adsorbed phase is in a similar condition to that under the standard state employed in the definition of the adsorption potential, or the one under the saturation concentration. It leads to the nitrobenzene- or benzonitrile-rich phase of the liquid-liquid equilibrium. Since the mutual solubilities of aromatic compounds are small in general, the composition of the phase could be approximated by the pure liquid. This situation can be understood on the basis of the solute-solvent interaction. A small mutual solubility means weak solute-solvent interaction and strong solute-solute interaction. With the aid of attracting force exerted by the solid, solute molecules can gather around the solid surface. Once solute molecules

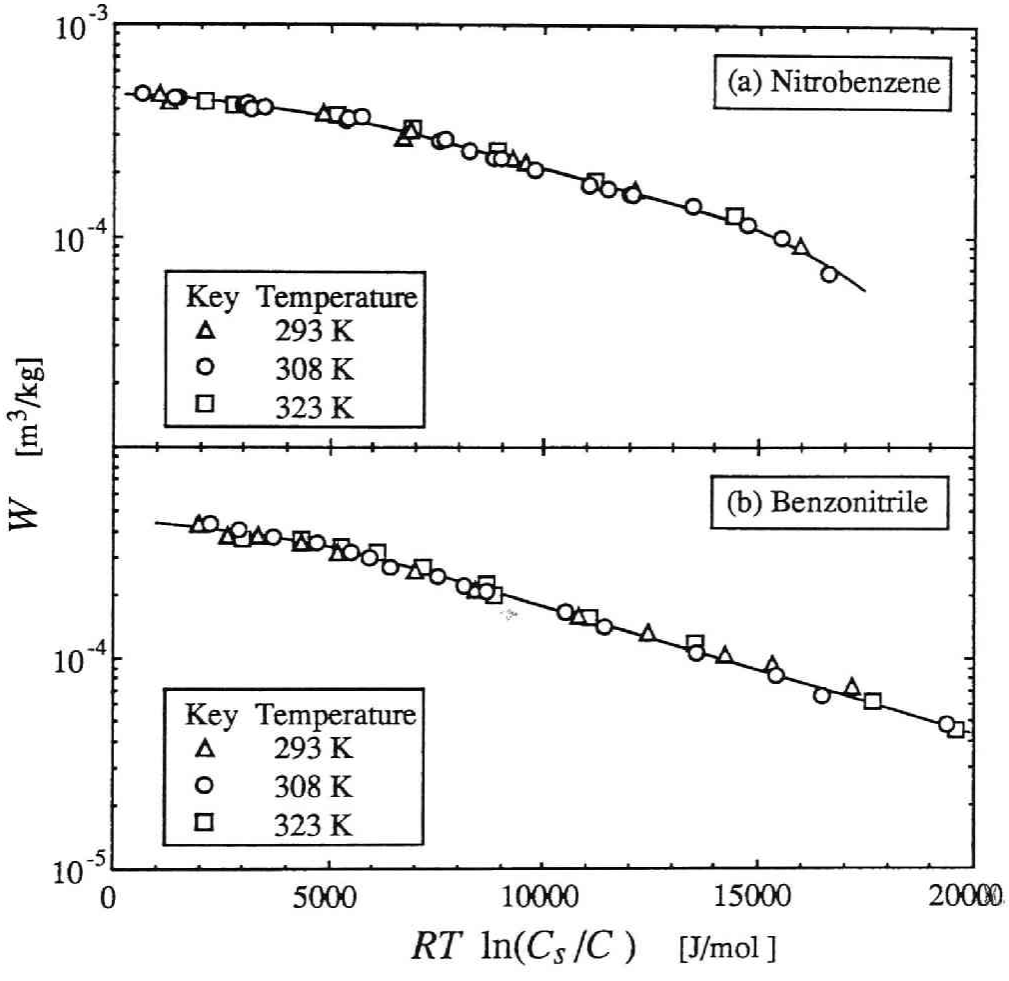

Figure 3.1. Potential plot of adsorption equilibrium
(a) for nitrobenzene and (b) for benzonitrile

get the chance to interact each other, this situation would be much 'comfortable' for them. Then, even if a solvent molecule, or a water molecule tries to be in the adsorbed phase, the adsorbed solute molecules do not allow the water molecule to be there. Thus the adsorbed phase could be nearly the pure liquid.

An example of the adsorbed state is illustrated in Figure 3.2(a). The adsorbed molecules can be assumed to exist as a *phase* within an equipotential surface in nearly the same thermodynamic condition as that of the pure liquid, rather than as localized molecules which specifically interact with the *adsorption sites* of the adsorbent.

2) Comparison with liquid phase ordinary diffusion In the interpretation of ordinary diffusion in liquid phase by this kind of hole model, the second elemental step mentioned above was found to have only a small activation energy compared with that for making a hole (Tyrrell, 1984). Based upon the discussion of the preceding section, this step can be assumed to have negligibly small energy of activation also in the adsorbed phase. Generation of the hole and succeeding movement of the molecule are illustrated in Figure 3.2(b). Hole generation in the solution contributes to the pore diffusion process or to a microscopic desorption process, while hole generation in the adsorbed phase is available to surface diffusion or to a microscopic adsorption. Hence, to be determined is *the free energy for making a hole in the potential field of adsorption* which is sufficient in size for an adsorbate molecule to accommodate itself, and its dependency on concentration. The rate constant k expresses the frequency of momentary holes generated by random motion of molecules in the phase. The energy for making such a hole is considered further in comparison with free liquid.

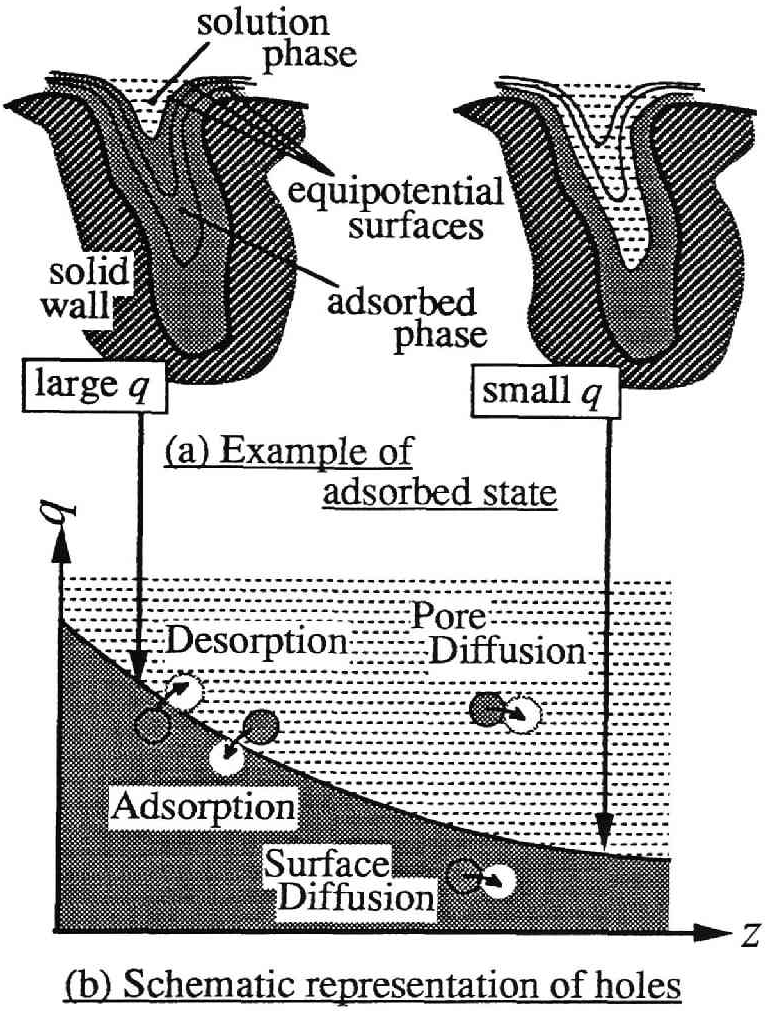

Figure 3.2. Adsorbed state and holes for movement of molecules

The energy needed to make a hole of the size of the volume per molecule in a phase of free liquid is equal to the evaporative energy per molecule (Glasstone *et al.*, 1964). It does not mean that the evaporation process will occur to make a hole. Rather, the evaporative energy appears because it is a measure of the interaction between the molecules. Then, the activation free energy for making a minimum-size hole for a molecule in free liquid can be a certain fraction of the evaporative energy, $a \cdot \Delta E_{vap}$ since the size of a hole for movement need not be the same size as the volume per molecule (Glasstone *et al.*, 1964). Extending this concept to adsorbed phase, the energy needed to make a hole of the size of the volume per adsorbate molecule in the adsorbed phase should be the evaporative energy of the adsorbate ΔE_{vap} *plus* additional energy ΔF_{ads} which arises from the fact that the phase is in a potential field of adsorption. In other words, it is more difficult to make a hole in the potential field because the adsorbent is attracting all the adsorbate molecules in the potential field. This additional energy should be equal to the attracting energy exerted by the adsorbent solid. Then, this should be equal to that needed to move the adsorbed phase to the state of free liquid, which is, by the definition, the adsorption potential itself. Finally, the activation free energy of surface diffusion can be expressed as a certain fraction of the sum of the two energy terms.

$$\Delta F^{\ddagger} = a\,(\Delta E_{vap} + \Delta F_{ads}) \tag{3.9}$$

3) Correlation equation for surface diffusivity Substituting Eq.(3.9) into Eq.(3.8),

$$u_a = u_{ao}^{*} \exp[\,-a\,(\frac{\Delta E_{vap} + \Delta F_{ads}}{RT})\,)] \tag{3.10}$$

$$= u_{ao}^{*} \exp(\,-a\,\frac{\Delta E_{vap}}{RT}\,)\left(\frac{C}{C_s}\right)^{a} \tag{3.11}$$

where

$$u_{ao}^{*} = \frac{\lambda^2}{\mu_s h} \tag{3.12}$$

$$\Delta F_{ads} = RT \ln(C_s/C) \tag{3.13}$$

Equation (3.11) says that u_a is logarithmically linear with liquid concentration at a given temperature. The same functional relation between u_a and C was derived in the preceding chapter. Combining Eq.(3.11) with Eq.(3.7), the surface diffusivity can be described by a power function of the amount adsorbed if the Freundlich isotherm holds.

The formula of Eq.(3.10), which has only 2 parameters, is thought to be appropriate for the correlation of concentration and temperature dependence. When logarithms of u_a's are plotted with $(\Delta E_{vap}+\Delta F_{ads})/RT$, a single line should be obtained for various temperatures since u_{ao}* is considered to have almost no dependence on temperature. Note that u_{ao}* depends on the combination of adsorbate and adsorbent while the ratio a might be unique only for adsorbate as far as the potential theory of adsorption holds.

3.4 Results and discussion

3.4.1 Performance of the equation

The obtained surface diffusivities are plotted against amount adsorbed in Figure 3.3 for nitrobenzene and benzonitrile, where the data at 308K shown in Chapter 2 are also plotted. As shown in the figure, the data show a sigmoid way of change for each adsorbate and at each temperature studied.

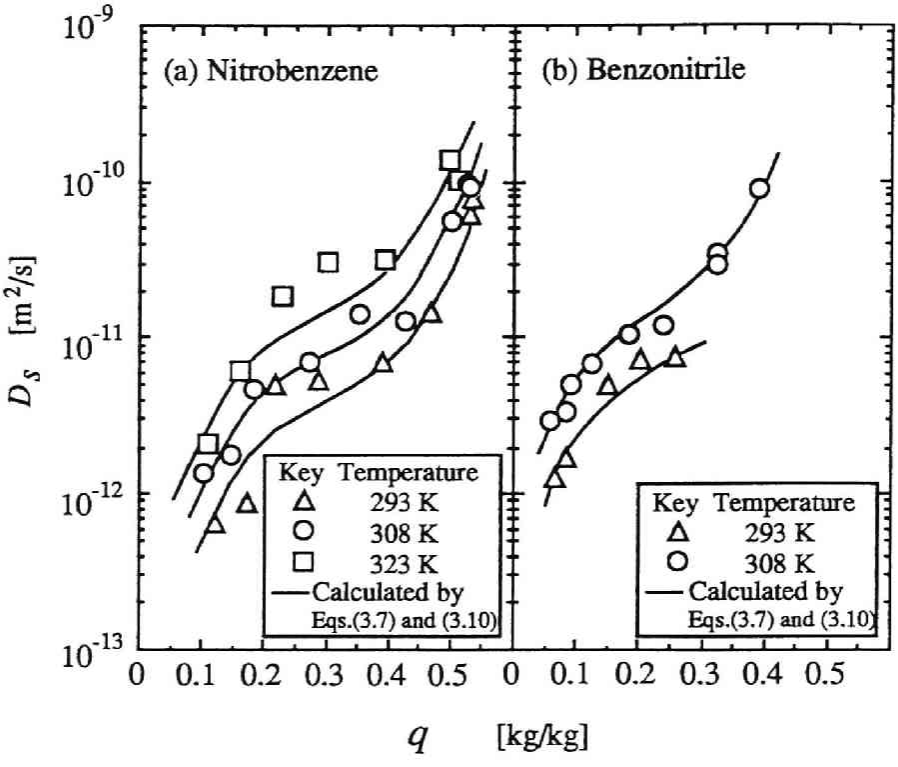

Figure 3.3. Relation between surface diffusivity and amount adsorbed
(a) for nitrobenzene and (b) for benzonitrile

As already shown in Figure 3.1, the adsorption isotherms have portions deviating from the Freundlich equation. Thus a correlation was tried using u_a rather than the diffusivity itself.

The D_S data were converted to the u_a's by Eq.(3.7), using the logarithmic slopes of the isotherms which were obtained from Figure 3.1. The quantitative test of Eq.(3.10) is shown in Figure 3.4 for nitrobenzene. A similar correlation for benzonitrile is shown in Figure 3.5. The physical properties used are summarized in Table 3.1. The data at different temperatures come close to a single line and no significant trends away from the correlating line can be distinguished in either case. Though we have to admit relatively large uncertainties in the logarithmic slopes of the adsorption isotherms, the linearities obtained are quite promising. The obtained parameters are

Nitrobenzene : $u_{ao}^{*} = 1.8\text{x}10^{13}$ m/(Ns), $a = 0.44$

Benzonitrile : $u_{ao}^{*} = 4.1\text{x}10^{13}$ m/(Ns), $a = 0.43$

These parameters are used to re-calculate the surface diffusivity as shown by the solid lines in Figure 3.3, which well explain both the concentration dependence and temperature dependence. The sigmoid change of D_S against q can now be understood as follows. Equation (3.11) reduces to a power function of q in the lower concentration range to yield a convex portion. The decrease in logarithmic slope of the isotherm in the higher concentration range results in the increase of D_S and in a small change of q against C. Thus D_S shows a steep rise against q.

The success in describing the temperature dependence is thought to be direct verification of the assumption employed in the formulation of the activation free energy. Note that the value $a(\Delta E_{vap}+\Delta F_{ads})$ is close to, or even greater

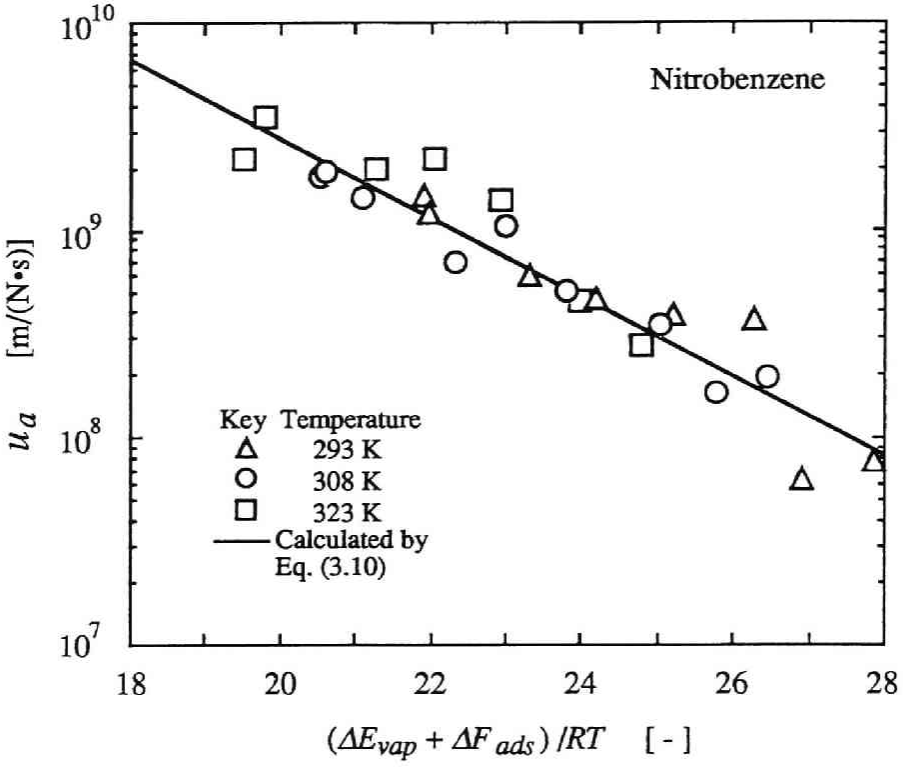

Figure 3.4. Correlation of u_a and energy term for nitrobenzene

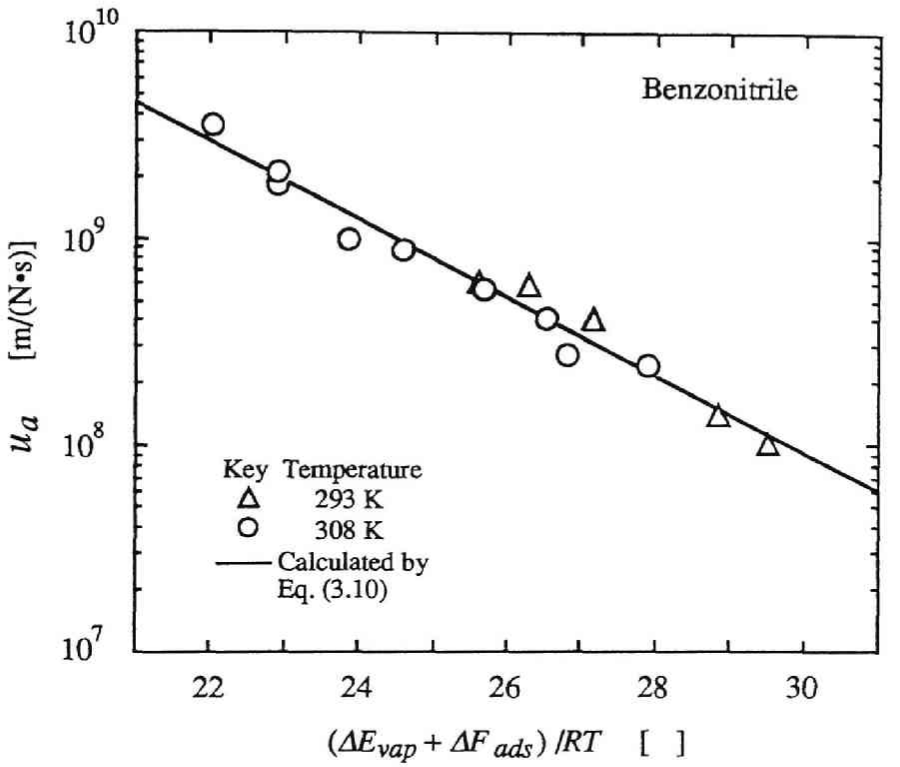

Figure 3.5. Correlation of u_a and energy term for benzonitrile

than, the isosteric heat of adsorption, which is approximately equal to ΔH_{sol} $+\Delta F_{ads}$ as shown in the preceding chapter.

3.4.2 Validity of the parameters

The parameter a shows the ratio of the energy for making hole for movement and the one needed for the size of volume per molecule. The two sizes differ from each other since the size of a hole for movement can be a minimum-size one and since the latter includes free volume. The parameter a should be a measure of the difference between the two sizes. The parameter can be compared with the result of viscosity of liquids analyzed with the absolute rate theory (Glasstone *et al.*, 1964). The ratios of activation free energy for viscosity and the evaporative energy were reported to be scattered mostly between 0.35-0.5. The average was 0.41 for about one hundred compounds (Powell *et al.*, 1941). Our results of 0.43-0.44 are in quite good accord with it.

By the definition of Eq.(3.12), the value of u_{ao}* could roughly be estimated. The distance of two neighboring equilibrium positions, λ, can be assumed to be about the same as the diameter of the adsorbate molecule. Accordingly, λ is calculated to be about 5-6x10^{-10} m according to estimation by $(v/N_A)^{(1/3)}$. The tortuosity for surface diffusion, μ_s, could be larger than that for pore diffusion. However, the value for pore diffusion measured in Chapter 2 is substituted here. The resultant estimates of u_{ao}* lie in the 9-20x10^{13} m/(Ns) range. Considering the degree of the estimation, the estimated and fitted values are fairly consistent with each other.

A fitted value smaller than the estimated one might have resulted from the neglect of the energy for the movement. The comparison of these two values allows us to calculate the *neglected* energy for the second step. It resulted in no more than 10% of the energy for the hole making step, similarly to the

situation often observed in molecular diffusion or viscosity in liquids[16]. Namely, the first step is thought to have major importance in surface diffusion in the systems studied here.

3.4.3 Accord with other research results

If the Freundlich isotherm holds, Eqs.(3.7) and (3.11) reduce to an expression of D_S by a power function of q. Hence the a's obtained here can be compared with the results obtained by Muraki *et al.* (1982) for aromatic compounds with Freundlich isotherms. They analyzed the concentration-time curves of kinetic experiments using virgin carbons numerically with the power function formula of D_S. The results are 0.48 to 0.50 for a's of three kinds of the compounds, which show no great discrepancy with the present results.

Their experiments were made at a fixed temperature. The physical properties such as solubilities and evaporative energies are not specified either in their article or other literature available. Thus, to the authors regret, a more detailed discussion cannot be made about, e.g., temperature dependence and parameter values. It should be noted, however, that the present correlation equation includes their correlation as a special case for the Freundlich isotherms. Thus their success in describing the rate process by the power function formula itself could corroborate the validity of the present correlation.

Besides the concentration dependence, the present correlation equation accords with the results of Suzuki and Kawazoe (1975), on the temperature dependence of D_S and the relevance of the heat of vaporization as follows. They measured averaged surface diffusivities of 15 organic compounds on an activated carbon, some of which were measured at different temperatures, and correlated all of them by the following equation.

$$D_s = 1.1\text{x}10^{-8}\exp(-5.32T_b/T) \quad [\text{m}^2/\text{s}] \tag{3.14}$$

Further, they replaced the boiling temperature by the heat of vaporization using Trouton's rule to obtain

$$D_s = 1.1\text{x}10^{-8}\exp(\ 0.5\Delta H_{vap}/RT\ ) \quad [\text{m}^2/\text{s}] \tag{3.15}$$

This equation apparently shows that the activation energy of surface diffusion is equal to half the heat of vaporization. Since the evaporative energy ΔE_{vap} is equal to ΔH_{vap}-RT, the above equation can also be expressed as

$$D_s = 6.7\text{x}10^{-9}\exp(\ -\ 0.5\Delta E_{vap}/RT\ ) \quad [\text{m}^2/\text{s}] \tag{3.16}$$

Equation (3.16) can be an approximated functional formula of the present correlation equation as explained below. ΔE_{vap} of nitrobenzene, for example, is about 50 kJ/mol while ΔF_{ads} lies around 10 kJ/mol. The variation of ΔE_{vap} over the various compounds is then far greater than the variation of ΔF_{ads} for each compound. Further, the difference in the logarithmic slope of the isotherm can be neglected since their correlation is over about three orders of magnitude. Thus Eqs. (3.10) and (3.7) reduce to Eq. (3.16) for such a correlation. Namely, the present correlation is considered to include the above equation.

For a more quantitative verification, the pre-exponential factor was estimated with the present correlation equation. Combining Eqs. (3.7) and (3.11), we have

$$D_s = k_B T \left(\frac{\partial \ln C}{\partial \ln q}\right)_T \left(\frac{C}{C_s}\right)^a u_{ao}^{*} \exp(\ -\ a\frac{\Delta E_{vap}}{RT}\ ) \tag{3.17}$$

In their experiments, reciprocal exponents ranged mainly from 1.2 to 5.5. As an representative value, 3 was adopted. The relative concentration ranges were mainly from 0.01 to 0.1 which gave an representative value of 0.05. Further, since many of the organics they used were substituted aromatics, u_{ao}* was supposed to have similar value to ones obtained in the present work. Thus an intermediate value of 3×10^{13} m/(Ns) was employed for the calculation. The resultant value of estimation for the pre-exponential factor is 9×10^{-9} m^2/s, which shows unexpectedly good agreement with their result expressed in the form of Eq.(3.16). This agreement emphasizes the validity and usefulness of the present correlation equation.

The present model is also in line with the result of Itaya *et al.* (1987) for adsorption of aqueous solution of organic compounds onto macroreticular adsorbents. They obtained larger activation energy for surface diffusion than expected from the isosteric heat of adsorption and suggested the importance of the hole-making step.

The larger activation energy for surface diffusion compared with the isosteric heat of adsorption might sound strange by the concept of hopping of adsorbed molecules proposed for gas phase proposed by, e.g., Higashi *et al.* (1963), Gilliland *et al.* (1974) and Okazaki *et al.* (1981), because the diffusing molecule would *desorb* from the adsorbent surface at that moment. The larger activation energy in liquid phase could, however, be possible if the significance of the hole-making process is taken into account. The energy is not concentrated onto one diffusing molecule but is needed for hole-making, which is a cooperative process of a number of molecules.

From the present correlation, an advantage of using an effective diffusivity based on the gradient of *concentration* might be withdrawn. Denoting the diffusivity D_C ,

$$J_t \equiv J_s = - D_c \frac{dC}{dz} \tag{3.18}$$

Then D_C is related with the D_S by

$$D_c = \rho_{app} (dq/dC)\, D_s \tag{3.19}$$

Substituting Eq.(3.7) and (3.11) with the Freundlich isotherm, the dependence of D_C on concentration is

$$D_c = D_c^{'} (C/C_s)^{1/n - 1 + a} \tag{3.20}$$

If a Freundlich exponent of 0.3-0.4 and the parameter a of 0.5 are substituted, the exponent of the concentration is -0.1 to -0.2. Thus D_C shows relatively small change, compared with that of the surface diffusivity, even with great change of concentration. Using this diffusivity, a constant value would be capable of expressing the whole course of adsorption.

3.5 Conclusions

Eyring's rate theory was applied to the elemental steps of surface diffusion with the assumption that the rate-controlling step is the hole-making step for systems under the potential theory of adsorption. The activation energy was found to be a certain fraction of the sum of the evaporative energy of adsorbate and the adsorption potential. The obtained correlation equation had only two parameters to represent both concentration and temperature effects.

The equation was tested with measured surface diffusivities to show a good correlation of the concentration dependence at different temperatures. The parameters obtained through the correlation were considered to be

reasonable, based upon their definition and/or the accord with other research results. The hole-making step is considered to have major importance in the surface diffusion of liquid phase studied in the present work.

Appendix

If the intensity factor q is in proportion to the activity and if the rate constant k has no distribution over q, the mass flux for this uniform system would be expressed with the mass flux forward ($J_{S,f}$) and backward ($J_{S,b}$) between two neighboring positions a distance of λ apart.

$$J_S = J_{S,f} - J_{S,b}$$
$$= \rho_{app}\lambda_z k\, q - \rho_{app}\lambda_z k\,(q + \lambda_z \frac{dq}{dz}) = -\rho_{app}\lambda_z^2 k\, \frac{dq}{dz} \qquad \text{(A-1)}$$

where λ_Z, the length of one movement projected on the macroscopic mass transfer axis z, is used instead of λ to account for the tortuosity of the surface. They have the following relation.

$$\lambda_z^2 = \lambda^2/\mu_s \qquad \text{(A-2)}$$

The non-ideality affects the free energy of activation depending on its direction. The derivation follows the treatment of molecular diffusion in concentrated solution with Eyring's rate theory (Glasstone *et al.*, 1964). The uniform system is considered first here. Because of the non-ideality, the difference in standard free energy between the two neighboring positions, ΔF arises as follows.

$$\begin{aligned} \Delta F &= \lambda_z RT \frac{d\ln\gamma_a}{dz} \\ &= \lambda_z RT \frac{d\ln\gamma_a}{dq}\frac{dq}{dz} \\ &\equiv 2\alpha RT \end{aligned} \tag{A-3}$$

where γ_a is the activity coefficient for adsorbed molecules. The activation free energy for forward movement would be equal to the one for ideal case plus the half of the difference derived above.

$$\Delta F_f^{\ddagger} = \Delta F^{\ddagger} + \frac{1}{2}\Delta F = \Delta F^{\ddagger} + \alpha RT \tag{A-4}$$

The backward one is similarly

$$\Delta F_b^{\ddagger} = \Delta F^{\ddagger} - \frac{1}{2}\Delta F = \Delta F^{\ddagger} \quad \alpha RT \tag{A-5}$$

The rate constants for forward and backward movements can be related with corresponding free energies similarly to Eq.(3.3).

$$k_f = \frac{k_B T}{h}\exp\left(-\frac{\Delta F_f^{\ddagger}}{RT}\right) = k\cdot e^{-\alpha} \tag{A-6}$$

$$k_b = \frac{k_B T}{h}\exp\left(-\frac{\Delta F_b^{\ddagger}}{RT}\right) = k\cdot e^{\alpha} \tag{A-7}$$

where k shows the rate constant for the ideal system which is identical with the one in Eq. (3.3). Thus the mass flux will be the difference between forward and backward movements.

$$\begin{aligned} J_s &= J_{s,f} - J_{s,b} \\ &= \rho_{app}\lambda_z k_f q - \rho_{app}\lambda_z k_b \left(q + \lambda_z \frac{dq}{dz}\right) \\ &= \rho_{app}\lambda_z k \left[q\left(e^{-\alpha} - e^{\alpha}\right) - e^{\alpha}\lambda_z \frac{dq}{dz}\right] \end{aligned} \tag{A-8}$$

α is thought to be far smaller than unity. Then the exponential terms can be approximated as

$$e^{-\alpha} \approx 1-\alpha\ ,\quad e^{\alpha} \approx 1+\alpha \tag{A-9}$$

Thus

$$J_s = -\rho_{app}\lambda_z k\,[2\alpha\, q + (1+\alpha)\lambda_z \frac{dq}{dz}] \tag{A-10}$$

Further, α of the second term in the brackets can be neglected compared with unity.

$$\begin{aligned} J_s &= -\rho_{app}\lambda_z k\,(2\alpha\, q + \lambda_z \frac{dq}{dz}) \\ &= -\rho_{app}\lambda_z^2 k\,(\frac{d\ln\gamma_a}{dq}q + 1)\frac{dq}{dz} \end{aligned} \tag{A-11}$$

The quantity in the parenthesis can be rearranged to yield

$$(\frac{d\ln\gamma_a}{dq}q + 1) = (\frac{d\ln\gamma_a}{d\ln q} + 1) = (\frac{d\ln a_a}{d\ln q}) = (\frac{d\ln a_i}{d\ln q}) \tag{A-12}$$

The derivative of activity of adsorbed phase, $d\ln a_a$, could be substituted by that in solution phase in equilibrium, $d\ln a_i$ The derivative should be the one at constant temperature. Strictly, then, it should be expressed in the form of partial derivative. Thus the flux will be

$$J_s = -\rho_{app}\frac{\lambda^2}{\mu_s} k \left(\frac{\partial \ln a_i}{\partial \ln q}\right)_T \frac{dq}{dz} \tag{A-13}$$

Comparing Eq.(A-13) with (A-1), it is clear that the effect of the non-ideality of the factor q appears as the additional term. Namely, we have to add the logarithmic derivative to account for the non-ideality. If we have a distribution on the rate constant, then the net mass flux can be expressed by

an integration with respect to q' from zero to the amount adsorbed at each location.

$$
\begin{aligned}
J_s &= J_{s,f} - J_{s,b} \\
&= \int_0^{q} \mathrm{d}J_s\,(q') - \int_0^{q+\lambda_z \frac{\mathrm{d}q}{\mathrm{d}z}} \mathrm{d}J_s\,(q') \\
&= -\rho_{app}\lambda_z \int_{q}^{q+\lambda_z \frac{\mathrm{d}q}{\mathrm{d}z}} k\,(q') \left(\frac{\partial \ln a_i}{\partial \ln q}\right)_T \mathrm{d}q' \qquad \text{(A-14)} \\
&= -\rho_{app}\lambda_z^2 k\,(q) \left(\frac{\partial \ln a_i}{\partial \ln q}\right)_T \frac{\mathrm{d}q}{\mathrm{d}z}
\end{aligned}
$$

Note that the frequency k at $q' = q$ appears here. Substituting Eq. (A-2), we finally obtain

$$
J_s = -\rho_{app} \frac{\lambda^2}{\mu_s} k\,(q) \left(\frac{\partial \ln a_i}{\partial \ln q}\right)_T \frac{\mathrm{d}q}{\mathrm{d}z} \qquad \text{(A-15)}
$$

which is identical with Eq.(3.4).

CHAPTER 4

CAPILLARY CONDENSATION IN LIQUID PHASE AND ADSORPTION ISOTHERM

4.1 Introduction

Pore sizes as well as the physico-chemical natures of solids play an important role in many fields such as physical adsorption, chemisorption and catalysis. In gaseous phase adsorption, the so-called Kelvin condensation, or capillary condensation may contribute to the amount adsorbed appreciably in higher range of the relative pressure, especially for mesoporous solids. The capillary condensation can be interpreted as follows: the vapor-liquid equilibrium of the adsorbate is deviated from that with a flat liquid surface by the curvature of the liquid surface which results from the contact with walls of the narrow pores. This phenomenon is reversely utilized for characterization of porous solids (e.g., Barrett *et al.*, 1951; Wheeler, 1955; Cranston and Inkley, 1957; Dollimore and Heal, 1964), especially in the mesopore range, which is now quite popular and getting more like a routine work. The effect of pore sizes on the adsorption in liquid phase, however, still remains unclear. Only a limited number of research results have lighted up the effect and hence almost no guideline has been established for the pore structure of an adsorbent in liquid phase adsorption.

A similar situation in liquid phase to the capillary condensation of gaseous phase may be as follows; a hindered liquid-liquid equilibrium could stand within a pore because of the presence of a curved interface of the two liquid phases. In other words, a solute-rich phase could be equilibrium with a

solvent-rich phase at a lower concentration than the saturated. Patrick and co-workers (Patrick and Jones, 1925; Patrick and Eberman, 1925) first suggested the possibility of this phenomenon and intuitively proposed a Kelvin-type equation for the relation between the pore radius and the concentration. However, no sound basis for derivation of the equation nor quantitative tests with experimental data were presented. In spite of its importance not only in the field of adsorption but also in many relevant fields, no significant advance seems to have been made since then. As the matter of fact, many prominent books on adsorption did not mention the phenomenon, except the one by Kipling (1965). As a result, the nature of this phenomenon remains unclear. Here the author calls this phenomenon "Capillary Phase-Separation (CPS)".

If such a solute-rich phase holds within a pore at a concentration less than the saturation, the apparent amount adsorbed in liquid phase consists of at least two *adsorption* modes, namely, one associated with the affinity for the surface itself and the other with the CPS. Hence the knowledge of the relation between the concentration and the curvature enables us to interpret the adsorption isotherms of adsorbates with limited solubilities onto porous solids to some extent, especially in higher range of relative concentration.

The purpose of this work has been to clarify the effect of pore characteristics of a solid on liquid phase adsorption isotherms for solutes with limited solubility, through a quantitative treatment of the relation between the curvature of the interface and the concentration. Further, utilizing this concept, a method to estimate liquid phase adsorption isotherms from the information of pore characteristics, especially from nitrogen isotherms, has been proposed. The method is successfully applied to adsorption isotherms of aromatic compounds from aqueous solution.

4.2 Liquid-liquid equilibrium with curved interface

Suppose that we have two equilibrium states including components A and B as shown in Figure 4.1, namely, one with a flat interface and the other with a curved one existing within a pore which has a cylindrical shape, as an example, with radius r. The interface with the interfacial tension σ contacts to the wall with the contact angle θ. The components A and B correspond to a solvent and an adsorbate, respectively, in the case of adsorption. Besides, α-phase corresponds to a bulk phase and β-phase contributes to the amount adsorbed.

The chemical potentials, μ, of each component in both states are considered with the following assumptions: Molar volumes, v, of dilute components are approximated as that of the infinite dilution, and those of concentrated components as that of pure states, and they are constant against pressure. Equating corresponding potentials, we obtain

$$\mu_A^o + v_A^o(P - P_o) + RT \ln a_{AS}^{\alpha} = \mu_A^* + v_A^*(P - P_o) + RT \ln a_{AS}^{\beta} \tag{4.1}$$

$$\mu_B^* + v_B^*(P - P_o) + RT \ln a_{BS}^{\alpha} = \mu_B^o + v_B^o(P - P_o) + RT \ln a_{BS}^{\beta} \tag{4.2}$$

$$\mu_A^o + v_A^o(P - P_o) + RT \ln a_A^{\alpha} = \mu_A^* + v_A^*(P' - P_o) + RT \ln a_A^{\beta} \tag{4.3}$$

$$\mu_B^* + v_B^*(P - P_o) + RT \ln a_B^{\alpha} = \mu_B^o + v_B^o(P' - P_o) + RT \ln a_B^{\beta} \tag{4.4}$$

where subscript S is pertaining to the standard state with flat interface and v's are molar volumes for which the superscript * is pertaining to dilute state and ^{o} to concentrated state. Subtracting Eq. (4.1) from Eq. (4.3)

$$RT \ln \frac{a_A^{\alpha}}{a_{AS}^{\alpha}} = v_A^*(P' - P) + RT \ln \frac{a_A^{\beta}}{a_{AS}^{\beta}} \tag{4.5}$$

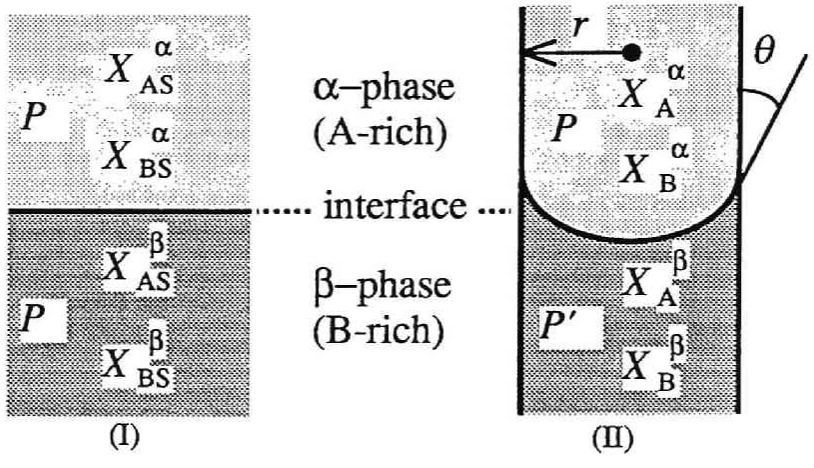

Figure 4.1. Liquid-liquid equilibria with flat and curved interfaces

Similarly from Eq. (4.2) and (4.4)

$$RT \ln\frac{a_B^{\alpha}}{a_{BS}^{\alpha}} = v_B^{o}(P' - P) + RT \ln\frac{a_B^{\beta}}{a_{BS}^{\beta}} \tag{4.6}$$

The mechanical balance of phases is expressed by Young-Laplace Equation.

$$P' - P = -2\sigma \cos\theta / r \tag{4.7}$$

For the activities, Raoult's law is assumed for concentrated components and Henry's law for dilute components. Then the ratios of the activities can be substituted by the ratios of mole fractions. Thus

$$\frac{X_A^{\alpha}}{X_{AS}^{\alpha}} = \frac{X_A^{\beta}}{X_{AS}^{\beta}} \exp(\phi_A) \tag{4.8}$$

$$\frac{X_B^{\alpha}}{X_{BS}^{\alpha}} = \frac{X_B^{\beta}}{X_{BS}^{\beta}} \exp(\phi_B) \tag{4.9}$$

where

$$\phi_A = \frac{2\sigma v_A^{*} \cos\theta}{r RT} \tag{4.10}$$

$$\phi_B = \frac{2\sigma v_B^{o} \cos\theta}{r RT} \tag{4.11}$$

Since $X_A{}^{\alpha} = 1 - X_B{}^{\alpha}$ and $X_A{}^{\beta} = 1 - X_B{}^{\beta}$, Equation (4.8) can be rearranged to be

$$X_B^{\beta} = 1 - (1 - X_B^{\alpha})\frac{X_{AS}^{\beta}}{X_{AS}^{\alpha}} \exp(\phi_A) \tag{4.12}$$

Substituting Eq. (4.12) into Eq. (4.9) and rearranging, we obtain the equation for the relation between the concentration and the curvature as follows.

$$\frac{X_B^{\alpha}}{X_{BS}^{\alpha}} = \frac{X_{AS}^{\alpha} - X_{AS}^{\beta}\exp(\phi_A)}{X_{AS}^{\alpha}X_{BS}^{\beta}\exp(\phi_B) \quad X_{BS}^{\alpha}X_{AS}^{\beta}\exp(\phi_A)} \tag{4.13}$$

Equation (4.13) corresponds to the Kelvin equation of gaseous phase. A rather complicated form is obtained because two components contribute to the phase equilibrium in liquid phase. For other shape of the pore, the corresponding curvature should be substituted for $2\cos\theta/r$.

To simplify Eq. (4.13), a few more assumptions are made: $\theta = 0$; the solubility of A in β-phase is small so that the ratio $X_B{}^{\beta}/X_{BS}{}^{\beta}$ is close to unity; the concentrations of B-component in α-phases are small so that the mole fractions are in proportion to concentrations. Then the ratio $X_B{}^{\alpha}/X_{BS}{}^{\alpha}$ can be approximated by the ratio of concentrations, C/C_S , or the relative concentration The resulting equation is

$$\frac{C}{C_s} = \exp\left(-\frac{2\sigma v_B^{o}}{r\,RT}\right) \tag{4.14}$$

Now we obtain the same equation as that proposed by Patrick and Eberman (1925). One has to be careful whether Eq. (4.14) holds in a given system. All the assumptions made above except the one related to the contact angle are valid if each phase can be treated as an ideal dilute solution. Hence, the equation is applicable to aqueous solutions of, for example, aromatic compounds or aliphatic compounds because they have quite small solubilities in general.

The derivation made so far is for liquid-liquid equilibrium. However, almost the same treatment could be made for solid-liquid equilibrium. In this case, β-phase consists of only B component in general. Then Eq. (4.14) might be applicable to solid-liquid equilibria as far as the concave interface as shown in Figure 4.1 and the mechanical balance between the phases hold. The applicability will be discussed later.

4.3 Estimation of liquid phase adsorption isotherms

The solute-rich phase of the hindered liquid-liquid equilibrium within a pore would be counted as adsorbed amount at a lower concentration than the saturated. Accordingly, the total amount adsorbed consists of two modes of *adsorption*, namely, the *real* adsorption which arises from physico-chemical nature of the adsorbent surface, and the apparent amount which arises from the pore characteristics of the adsorbent especially in the mesopore range. This concept is quite the same as that employed in pore analysis of mesoporous solids by physisorption of gas. The two adsorption isotherms, namely, the isotherm in liquid phase and that in gaseous phase can now be connected by the pore size distribution function. Hence, a liquid phase adsorption isotherm can be estimated by taking the reversed procedure of pore analysis starting from the pore size distribution.

Among the existing pore analysis methods, the one proposed by Dollimore and Heal (1964) was used to determine the distribution in this study. The determined distribution should be recognized as an *effective* pore size distribution because the pores may not be cylindrical as assumed.

For the estimation of liquid phase isotherms, the information of the amount of the *real* adsorption is needed. This amount could be measured by adsorption experiments employing a non-porous solid. However, only a limited number of the measurements have been made so far, especially in higher range of relative concentration, as reported by Valenzuela and Myers (1989). It would be convenient if this amount could be expressed by a simple equation with less number of unknown parameters. Among the existing equations for surface adsorption (e.g., Frenkel, 1946; Halsey, 1948; Jura and Harkins, 1944), the amount was assumed to follow Frenkel-type formula.

$$t = t_o \left[\ln \frac{X_{BS}^{\alpha}}{X_B^{\alpha}} \right]^{-1/3} \cong t_o \left[\ln \frac{C_s}{C} \right]^{-1/3} \tag{4.15}$$

The equation is thought to be appropriate for a solute with non-specific interaction, e.g., van der Waals forces. For a solute with specific interaction with surface, Eq. (4.15) may fail to express the real adsorption. The validity of this formula was examined using graphite as a non-porous solid and will be discussed later.

Since the pore size calculation from nitrogen adsorption also gives the surface area distribution, the amount adsorbed on surface of a given range of pore radius can be calculated with the available area and Eq. (4.15).

Using Eq. (4.15), we have only one unknown parameter, t_O, for the estimation of liquid phase adsorption isotherms from the pore size distribution function. Hence, in principle, the unknown parameter can be determined if we have only one measured datum of the amount adsorbed in a liquid-phase adsorption system considered. Thus the entire isotherm for the system could be estimated. The t_O value might be unique for a given

combination of solution and base material of adsorbent by definition. The characteristics of the parameter will be discussed later.

The liquid phase adsorption isotherms were estimated with the reversed procedure of the pore analysis of Dollimore and Heal (1964). It is briefly explained below. The CPS phase could be approximated as a pure phase of adsorbate in this calculation because of the small solubility of water into the β-phase. A postulated value of t_O enabled the following calculation. The calculation started from a saturated state in which all the pores were filled with adsorbate. The pore size distribution obtained from nitrogen adsorption consists of some groups of pores with finite ranges in pore radius. First, the group of pores with the largest radii was subjected to consideration to give a calculated point of adsorption isotherm, at which this group of pores had no CPS phase and the real adsorption only existed. Other groups of pores, with smaller radii, had CPS within the pores. The concentration corresponding to this condition could be calculated since the lower limit of the pore radius of this group, r_{p1}, should satisfy the equation,

$$r_{p1} = r + t \tag{4.16}$$

and since both the critical radius r and the thickness t are function of the concentration as given by Eqs. (4.13) or (4.14) and (4.15). The amount adsorbed at this concentration could be calculated by knowing the difference from the saturation, ΔV_1, which should be the volume of the CPS phase in this range of pores, $\Delta V_{C\,1}$.

$$V_1 = V_{sat} - \Delta V_1 = V_{sat} - \Delta V_{c\,1} \tag{4.17}$$

The corresponding mass was calculated using the density of the adsorbate.

The second point could be calculated similarly but the procedure was somewhat complicated because the difference in the surface adsorption in the first group of pores $\Delta V_{S\,1}$ contributed to the total difference in addition to the volume of the CPS phase in the second group of pores.

$$V_2 = V_1 - \Delta V_2 = V_1 - (\Delta V_{c\,2} + \Delta V_{s\,1}) \tag{4.18}$$

Similarly, we could calculate the (i+1)-th point from the volume of CPS phase in the (i+1)-th group of pores $\Delta V_{C\,i+1}$ and the difference in surface adsorption in larger pores $\Delta V_{S\,i}$.

$$V_{i+1} = V_i - \Delta V_{i+1} = V_i - (\Delta V_{c\,i+1} + \Delta V_{s\,i}) \tag{4.19}$$

As the calculation proceeded, ΔV_{Si} consisted of more number of contributions since pores only with the surface adsorption increased. The calculation proceeded until the concentration became small enough so that the CPS phase would not contribute to the amount adsorbed, usually around $C/C_S = 0.2$. Note that the estimated isotherms consist of discrete points since the calculation procedure is based on the discrete data points of pore size distribution. For more details, the pore size calculation by Dollimore and Heal (1964) should be referred.

The t_O was chosen to show the best fit of the calculated isotherm to the experimental data. The validity of thus determined value of t_O is discussed later.

4.4 Experimental

The physical properties of the adsorbates used are summarized in Table 4.1. In addition to the four adsorbates which have liquid-liquid equilibrium with

Table 4.1 Physical properties of adsorbates

Adsorbate	Molecular weight [kg/mol]	Density[a] [kg/m3]	Interfacial tension with water phase[b] [N/m]	Saturated conc. with water[c] [mol%]
Nitrobenzene	123.11 x10^{-3}	1.19 x10^{3}	25.7 x10^{-3}	0.0320
Benzene	78.11 x10^{-3}	0.86 x10^{3}	34.1 x10^{-3}	0.0422
Aniline	93.13 x10^{-3}	1.01 x10^{3}	5.8 x10^{-3}	0.768
Benzonitrile	103.12 x10^{-3}	0.99 x10^{3}	28.0 x10^{-3} [d]	0.084[f]
Benzoic Acid	122.13 x10^{-3}	1.32 x10^{3}	22.2 x10^{-3} [e]	0.072[b]
p-Nitrotoluene	137.13 x10^{-3}	1.16 x10^{3}	26.9 x10^{-3} [e]	0.0065[f]

a) Daubert and Danner (ed.), 1985. b) Hata (ed.), 1984. c) Sørensen and Arlt, 1979. d) Reddy Karri and Mathur, 1988. e) estimated by the method of Nakai, 1969. f) measured in this work

water, benzoic acid and p-nitrotoluene were used to examine the applicability of the method to solid solutes. The reagents of research grade provided by Wako Pure Chemicals Inc. were used with no further purification. The adsorbents are also summarized in Table 4.2. The SP's, whose chemical structure is of stylene-divinylbenzene block co-polymer, and EC's, electric conductive porous carbonblacks, are typical mesoporous solids. So the CPS would show a large contribution for these adsorbents. In addition to porous adsorbents of different origin, a non-porous solid was employed to examine the validity of using Eq. (4.15) for the statistical thickness of the adsorbed layer in liquid phase. Before experimental usage, the carbonaceous adsorbents were washed with distilled water and evacuated at 383K for 24 hours while the macroreticular adsorbents were washed first with methanol before done with distilled water, and then evacuated at 333K for 48 hours.

The measurement were made by a batch adsorption method. The adsorbent was added to 300 ml solution in an Erlenmeyer flask stopped by Teflon-sealed screw cap to prevent solutes from evaporative loss. The flask was shaken in a thermostatted bath for 7 days. The initial and equilibrium

Table 4.2 Physical properties of adsorbents

Adsorbent	Class	Nitrogen surface area [m^2/kg]	Pore volume [m^3/kg]
EC	Porous	670×10^3	0.72×10^{-3}
EC600JD	carbonblack	1100×10^3	1.32×10^{-3}
SP900	Macroreticular	580×10^3	0.84×10^{-3}
SP206	adsorbent	430×10^3	0.42×10^{-3}
LGK-1	Activated	1000×10^3	0.55×10^{-3}
LGK-3	carbon	1460×10^3	0.84×10^{-3}
Graphite	Nonporous carbon	9.9×10^3	

concentration was determined by an ultraviolet spectrophotometer (Shimadzu UV-260). The amount adsorbed was calculated by a mass balance: $q = L\,(C_i - C)/W_a$.

Nitrogen adsorption isotherms at 78K were measured by an automated sorption measuring apparatus, BELSORP produced by Bel Japan, Inc. The principle of the measurement was the volumetric method. A review for such instruments is given by Mikhail and Robens (1983).

4.5 Results and discussion

4.5.1 Estimation of liquid phase adsorption isotherms

The pore size distributions of the adsorbents were determined from nitrogen adsorption isotherms as shown in Figure 4.2. All the porous solids more or less showed hysteresis. The distributions shown in the figure were calculated using adsorption branches of the isotherms. The question, which branch to use for pore size calculations, has been under discussion for many years. However, the purpose of the calculation made here is not to determine the pore size distribution itself but to obtain information for the estimation of

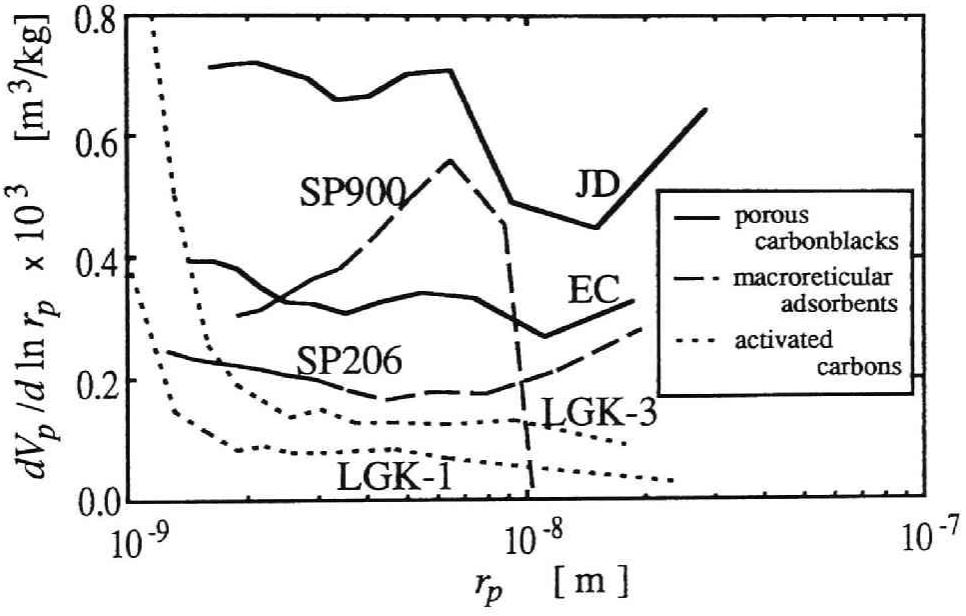

Figure 4.2. Pore size distributions from nitrogen adsorption

liquid phase adsorption isotherms. The adsorption branches of the hysteresis were used here for the 'pore size' calculation since liquid phase adsorption isotherms in general are considered to be that of adsorption branch of the hysteresis, if any. The obtained distribution should be considered as a projection of the nitrogen isotherm which reflects adsorption characteristics related to pore structure of the adsorbent. We could at least expect from Figure 4.2 that the CPS phase would contribute to the amount adsorbed for the porous carbonblacks and the macroreticular adsorbents since they had relatively large distribution in the so-called mesopore range.

The experimental and estimated results of the adsorption of nitrobenzene from aqueous solution onto porous adsorbents are shown in Figures 4.3 - 4.5. Each figure shows the results of two solids of different pore characteristics but of the same origin. Separate determinations of t_O for two solids of a group showed similar values to each other. Then, a common value of the parameter t_O was used for each group of adsorbents of the same origin. The solid lines show the estimated results based on the present method while the broken lines, for reference, show estimation using Eq.(4.15) only. As seen from the figures, the solid lines agree fairly well with the experimental data of various kinds of the adsorbents to show the validity of the method proposed.

The significance of the contribution of CPS is demonstrated in more detail in Figure 4.3a, in which some other broken lines with different value of t_O were calculated. As seen, the surface adsorption alone could not explain the steep rise of the experimental data. Attempts with surface adsorption alone failed similarly in other systems though only one broken line is shown in the figures.

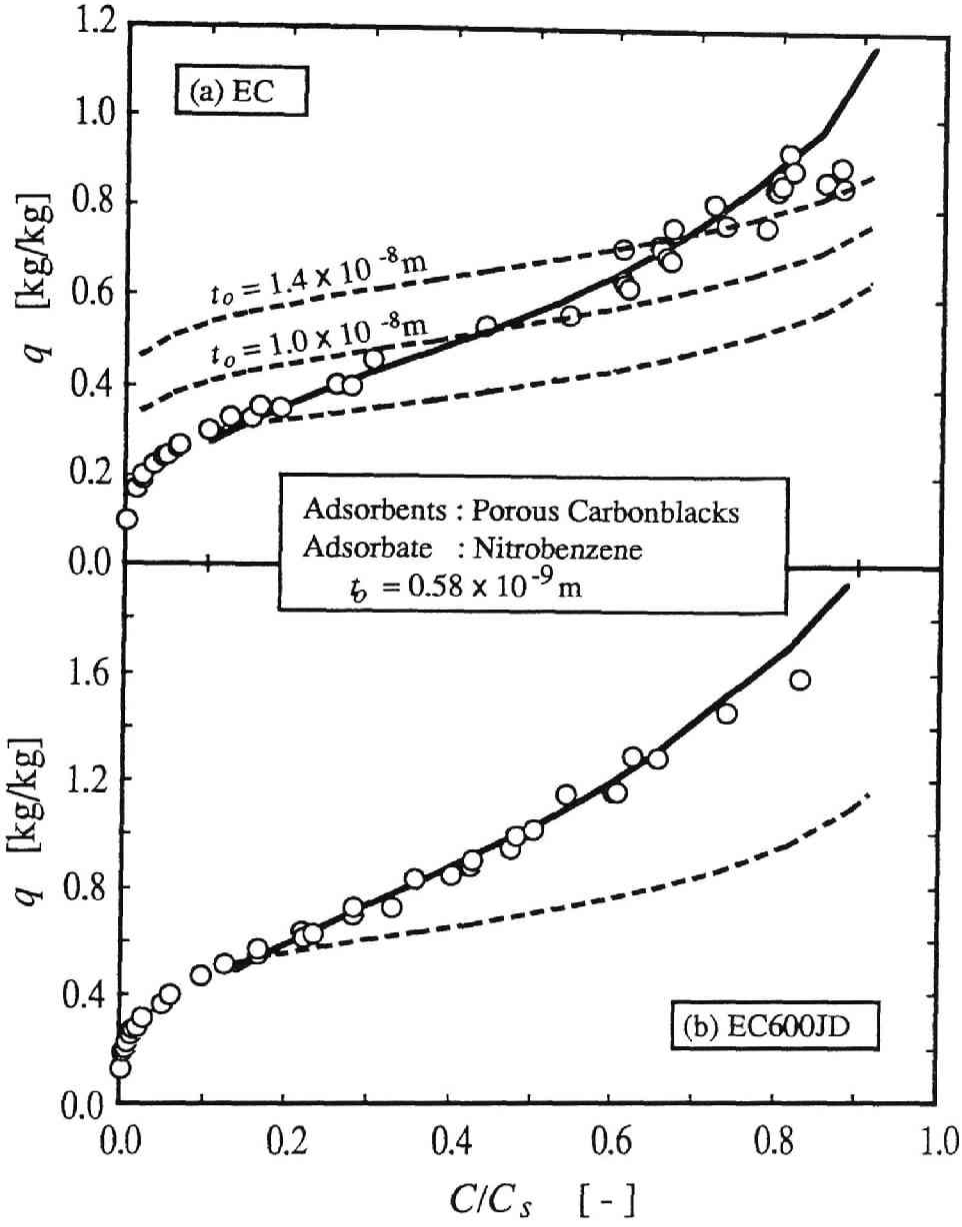

Figure 4.3. Adsorption isotherms for nitrobenzene from aqueous solution onto EC's

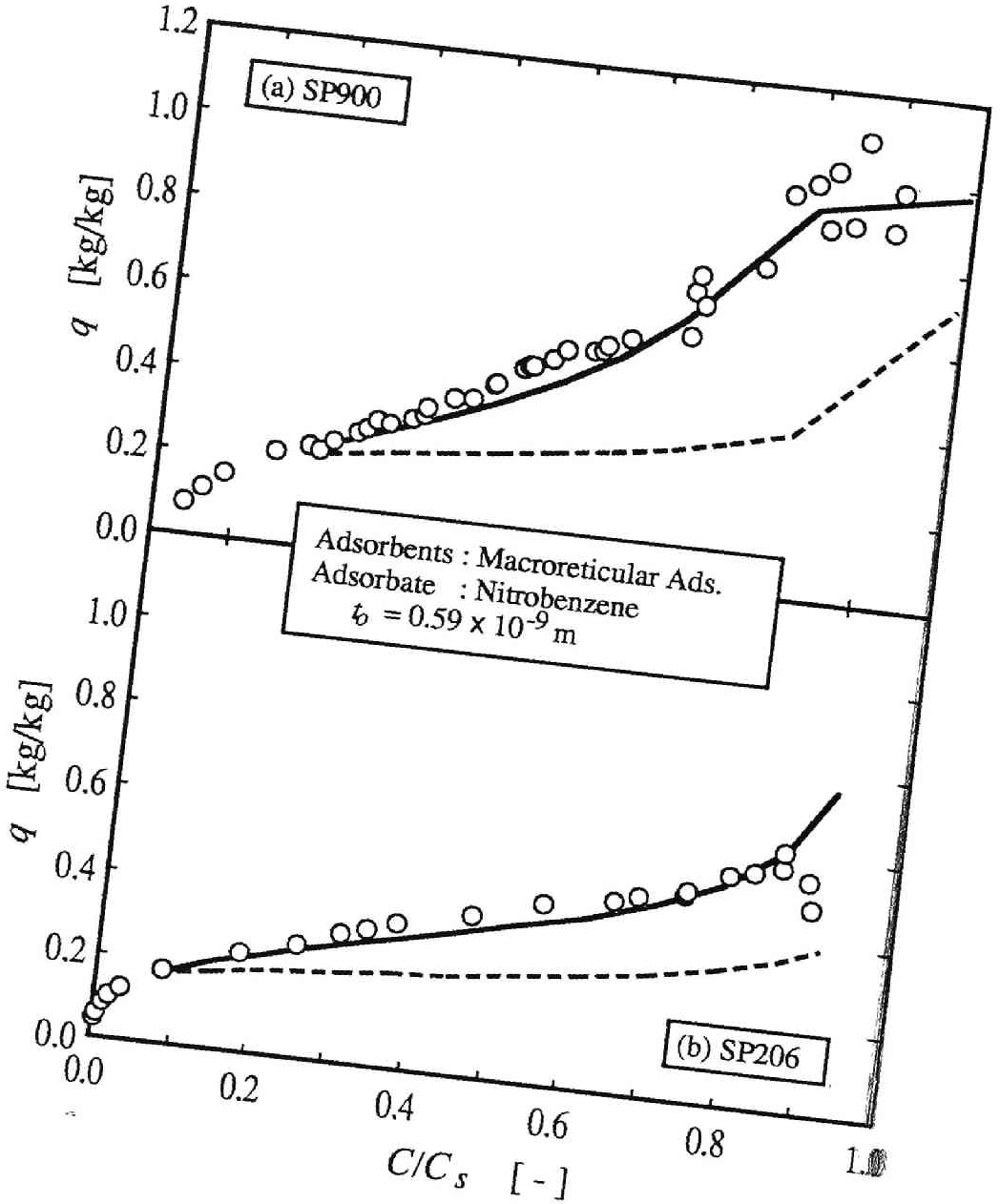

Figure 4.4. Adsorption isotherms for nitrobenzene from aqueous solution onto SP's

EC600JD in Figure 4.3b has almost twice larger pore volume than EC, which resulted in almost twice larger amount of adsorption from solution. Here a single value of t_O is surely enough for the two sets of experimental results of different pore size distributions with same chemical composition.

A similar result was obtained for macroreticular adsorbents as shown in Figure 4.4. This pair of porous solids have a rather distinct difference in the pore size distribution as shown in Figure 4.2. The success in the estimation well demonstrates the validity of the present method. Though the base material of the adsorbents which consists of aromatic rings and aliphatic chains is quite different from that of EC's in the sense of Carbon/Hydrogen ratio, the t_O value is quite close to that of EC's.

As for activated carbons, a strongly activated one, LGK-3, was used in addition to its original one, LGK-1. Because of increased mesopore volume LGK-3 shows a greater change of amount adsorbed than LGK-1 in Figure 4.5. It should be noted here that the broken lines lie below the solid lines because the broken lines show the contribution of the surface adsorption and are not comparable ones with the "standard isotherms" as in the t -plot by Lippens and de Boer (1965) and α_S-plot by Sing (1970).

The t_O obtained here shows just the same value as that of EC's. This result is quite reasonable because EC's and LGK's are supposed to have quite similar chemical composition. The estimation was successful also for this kind of solids. However, one problem on applying the method to activated carbons should be pointed out here.

The concept of the capillary phase-separation is based on an interpretation of the liquid-liquid equilibrium with the classical thermodynamics. It explains equilibrium between phases divided by a well-defined interface. We should

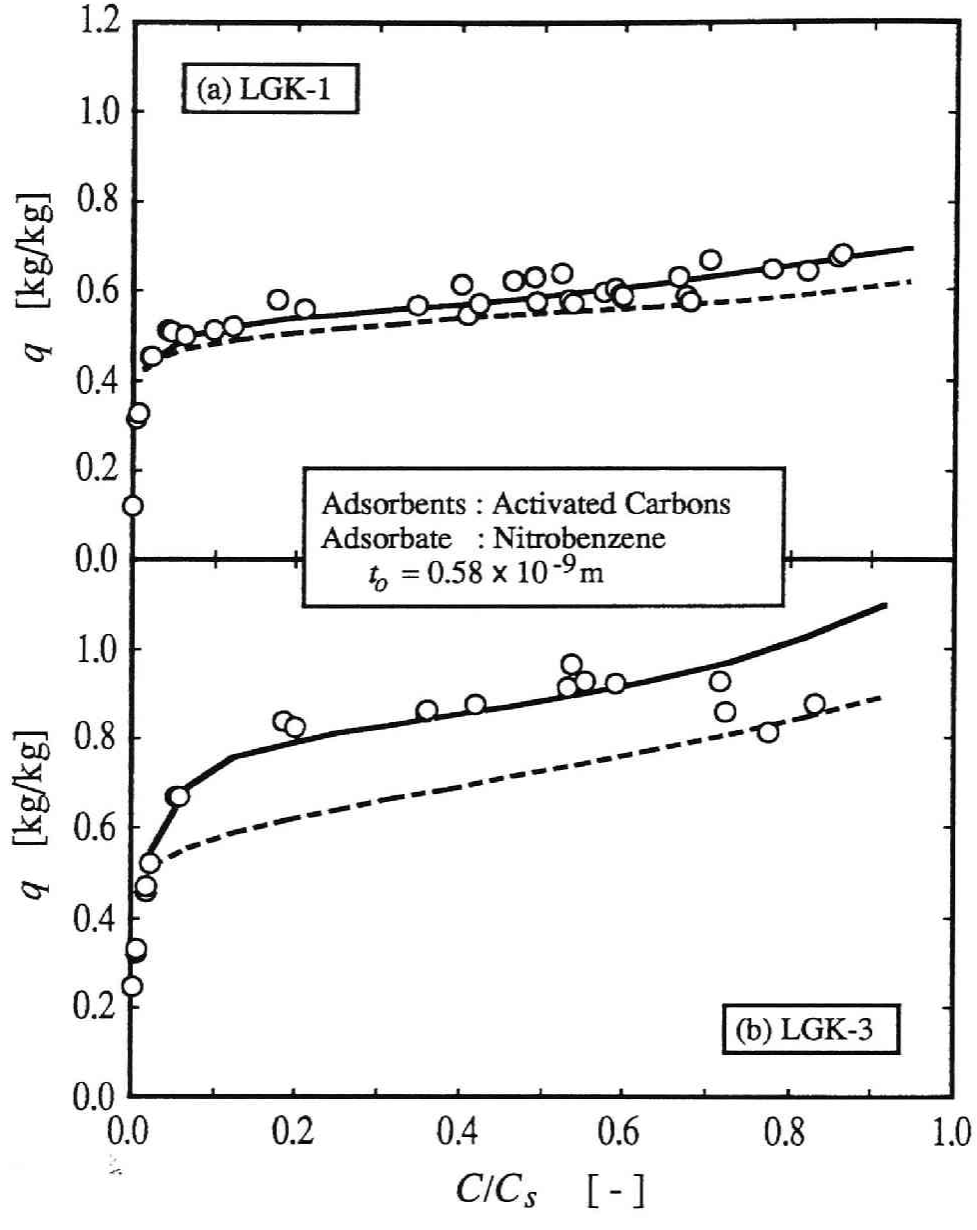

Figure 4.5. Adsorption isotherms for nitrobenzene from aqueous solution onto LGK's

not extend this concept into a pore of the so-called micropore range because a group of molecules can no more form a clearly determined interface to show its interfacial tension in such a narrow pore. Hence, the contribution of the CPS is limited to the mesopore volume of a given adsorbent. As expected, the contribution of the CPS was small for activated carbons as shown in Figure 4.5, which resulted in small changes of the amount adsorbed in the concentration range considered. The method provides relatively small advantage for such microporous solids though the estimated results agreed well with the experimental data. For mesoporous solids, on the other hand, the amount adsorbed varied significantly in the concentration range as shown in Figures 4.3 and 4.4. The method is of greater practical use for these kinds of adsorbents.

Other than nitrobenzene, three more solutes were used as adsorbates, whose adsorption isotherms onto porous carbonblack EC were obtained as Figures 4.6 - 4.8. Since the experimental data for benzene were rather scattered, because of the high volatility of the solutes, quantitative validity of the method was not clear in this case. However, the estimated curve followed experimental data qualitatively at least.

The estimation was made only above C/C_S = ca.0.5 in the case of aniline as a solute as shown in Figure 4.7. The interfacial tension of aniline-water system is very small compared with other systems examined here. A small interfacial tension in Eq. (4.13) or (4.14) brings the critical radius small at a certain relative concentration. As a result, the mesopore region corresponds to a higher range of the relative concentration in this system. The agreement between the solid line and the data was fairly good though the contribution of the CPS was relatively small.

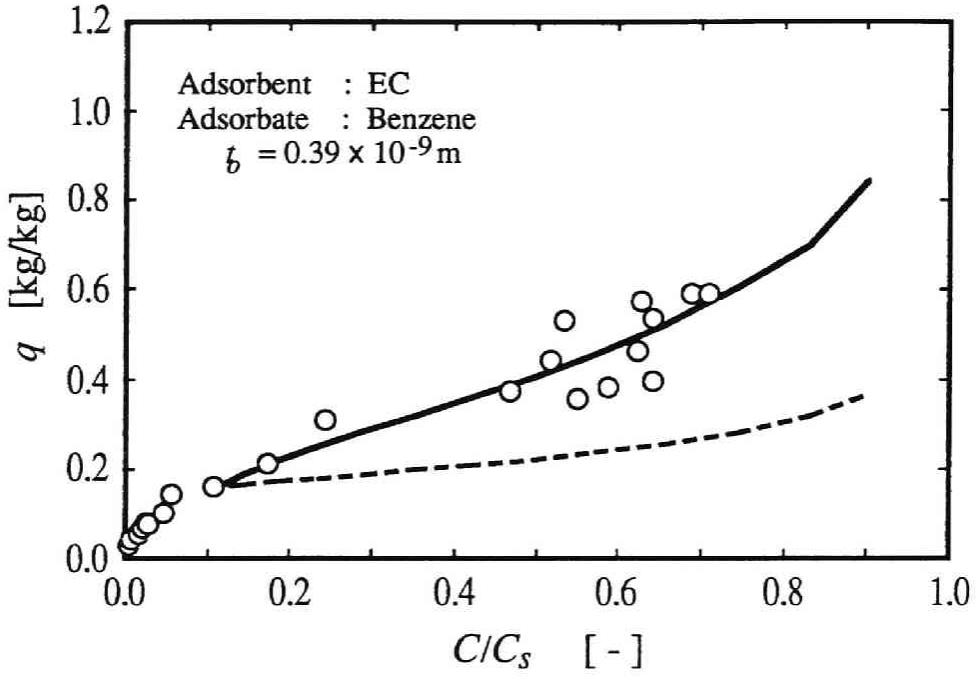

Figure 4.6. Adsorption isotherm for benzene from aqueous solution onto EC

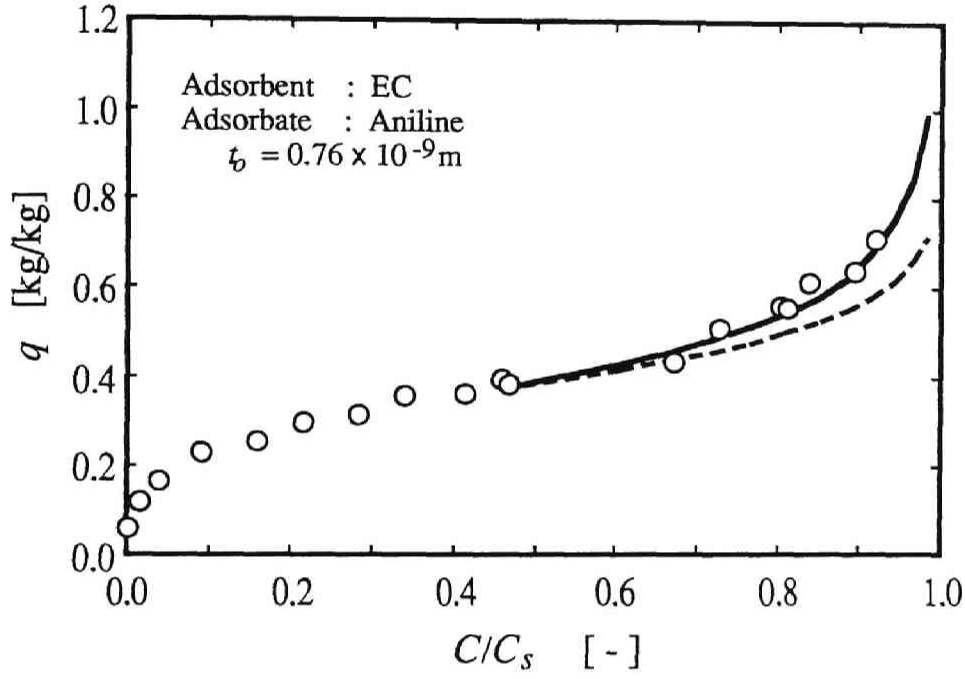

Figure 4.7. Adsorption isotherm for aniline from aqueous solution onto EC

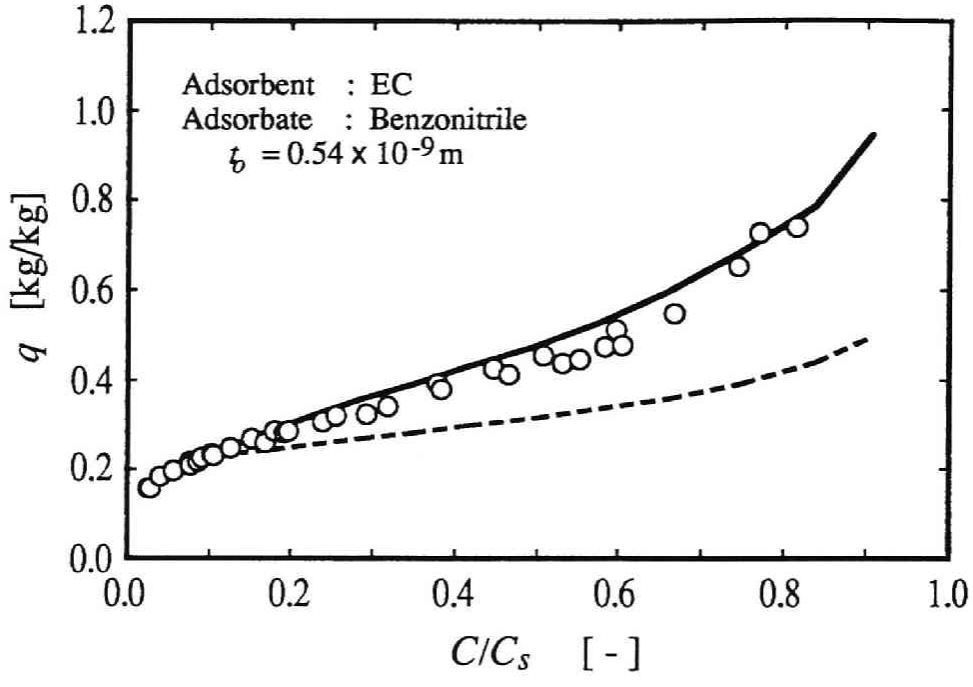

Figure 4.8. Adsorption isotherm for benzonitrile from aqueous solution onto EC

The present method was also successfully applied to the adsorption of benzonitrile solution onto EC as seen in Figure 4.8. From Figures 4.3(a) and 4.6 4.8, the applicability of the present method was confirmed for the adsorption of four different liquid solutes from aqueous solution onto the porous carbonblack EC.

4.5.2 Applicability to solid solutes

A reduction of solubility for solid solutes expressed by Eq. (4.14) can easily be expected when considering the situation with reversed curvature; a fine particle or an embryo shows greater solubility than sufficiently large one as often discussed in the field of precipitation. The greater solubility comes from a Kelvin effect which is similar to a larger vapor pressure of fine drops of liquid. Reversely then, a solid with concave interface might have smaller solubility than that with flat interface and thus yield a phase separation in a pore at a smaller concentration than the saturated.

The results of Figure 4.9, then, should be subjected to much discussion, which shows the isotherms for solid solutes as adsorbates onto porous carbonblack EC. Any attempt of calculation with CPS phase showed qualitative disagreement with the measured data. An example of the calculation is shown by the solid lines in the figure which were fitted to the data only in lower range of the relative concentration where the CPS phase would not contribute to the total amount adsorbed. This means that the amount adsorbed would increase as shown by the solid lines if the CPS phenomena would occur in these systems. However, the experimental data obviously deviate from the solid lines and are rather close to the broken line, which was calculated without CPS phase. The interfacial tensions were based on an estimation method (Nakai, 1969) and inevitably include some error. However, this magnitude of discrepancy cannot be attributed to the error in this property.

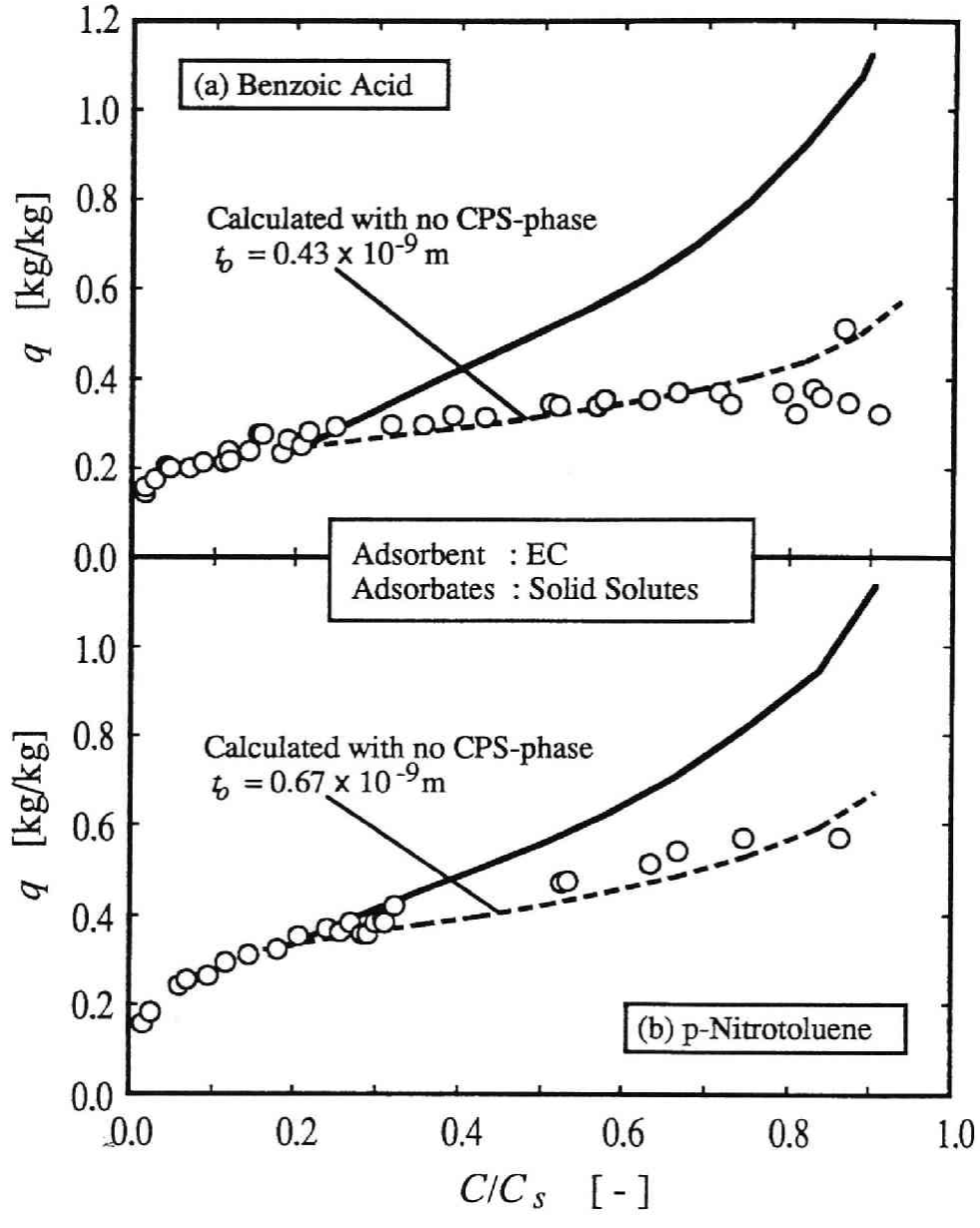

Figure 4.9. Adsorption isotherms for solid solutes from aqueous solution onto EC

The solid-liquid equilibrium with curved interface could be expressed by Eq. (4.14) as far as the concave interface and the mechanical equilibrium through the interface were valid. The discrepancy would tell us that either the shape of the interface or the mechanical balance is, or both of them are, not valid for solid solutes. The mechanical balance might be more complicated because a solid phase could stand with internal stress, which would affect the pressure in the solid phase. As a result, the method is not applicable to the adsorption of solutes with solid-liquid equilibrium. However, it should be noted that a solid solute may have a liquid-liquid equilibrium with a certain solvent as seen in phenol-water system. In that case, the method is thought to be applicable.

4.5.3 Parameter for statistical thickness of adsorbed phase

The verification of Eq.(4.15) as an expression for the *real* adsorption amount in liquid phase was tried with non-porous solid. The result of adsorption isotherm of nitrobenzene from aqueous solution onto graphite is shown in Figure 4.10. The broken line shows Eq.(4.15) with t_O value of 0.58 nm, which is the one obtained from the estimation for the nitrobenzene-EC system. Though the data were rather scattered because of the only small adsorption amount in this system, the broken line expresses the data fairly well in most part of the concentration examined. In lower concentration range, Eq.(4.15) overestimates the amount adsorbed to some extent. The important information for the estimation of liquid phase adsorption isotherms is the *real* adsorption amount in middle or higher range of the relative concentration. This characteristic of the present method would make the influence of the overestimate quite small. As a whole, the utilization of the Frenkel formula for the adsorption on surface is appropriate for the present method.

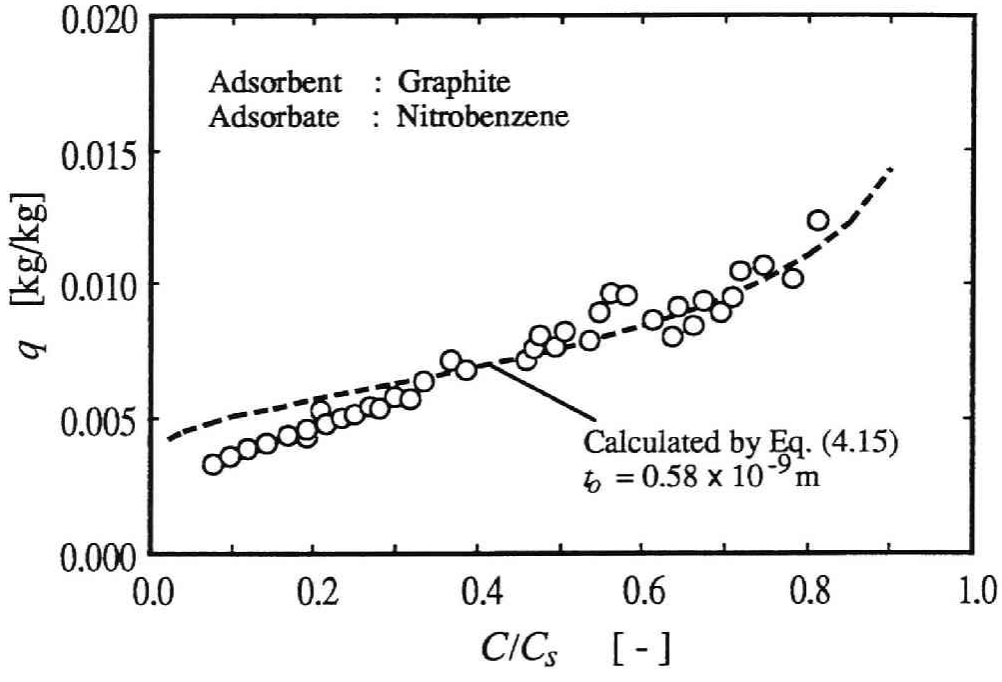

Figure 4.10. Adsorption isotherm for nitrobenzene from aqueous solution onto graphite

Table 4.3 Values of t_O

Adsorbate	Adsorbent	t_O [nm]
Nitrobenzene	EC EC600JD	0.58
	SP900 SP206	0.59
	LGK-1 LGK-3	0.58
Benzene	EC	0.39
Aniline		0.76
Benzonitrile		0.54

The obtained t_O values through the estimation for various combinations of adsorbent and adsorbate are summarized in Table 4.3. The variation of the value is quite small for an adsorbate, nitrobenzene, over the adsorbents used, while it shows relatively large variation over four kinds of adsorbates.

The insensitivity of the t_O value to the adsorbents may be interpreted as follows. In the concentration range studied here the apparent coverage exceeds unity, which implies more opportunity for an adsorbed molecule to interact with other adsorbed molecules. This situation for the molecule reduces the importance of the interaction with the solid surface. As a result, the influence of the adsorbent-adsorbate interaction on the t_O value becomes less important and the adsorbate-adsorbate interaction principally determines the t_O. If a unique value could exist for a given adsorbate, which can be applied to a relatively wide variety of solids, the estimation of liquid phase adsorption isotherms could be made without any measured data in liquid phase. It would need only the information of the nitrogen isotherms. Direct measurements of liquid phase adsorption on non-porous solids, however, would be needed to clarify the characteristics of the parameter in more detail.

Other than *a priori* estimation of the liquid phase adsorption isotherm, the knowledge of the parameter t_O enables us to follow the reversed procedure starting from a liquid phase adsorption isotherm to obtain the pore size distribution of the solid in liquid phase. As seen in macroreticular adsorbents, some porous materials swell or shrink when immersed in a solvent. Conventional methods such as the nitrogen adsorption and mercury immersion need evacuation before the measurement. The swollen or shrunk state in a solvent could not be obtained by these methods. Utilization of the CPS concept may enable us to obtain an *in situ* measurement of the pore characteristics of these kinds of porous solids. The possibility will be examined in the next Chapter.

4.6 Conclusions

The relation between the curvature of an interface of liquid-liquid equilibrium and the equilibrium concentration was derived. The relation suggested the existence of a solute-rich phase within a pore even at a lower concentration than the saturated. On the basis of this concept, a method to estimate liquid phase adsorption isotherms of a solute with limited solubility was proposed. Liquid phase adsorption isotherms of six kinds of solutes from aqueous solutions onto three categories of solids were measured. The comparison of estimated and experimental adsorption confessed fairly good applicability to liquid solutes and implied non-presence of CPS phenomena for solid solutes investigated. Further, utilizing this concept, we have a possibility to obtain pore characteristics of swollen or shrunk solid immersed in a solvent.

CHAPTER 5

IN-SITU CHARACTERIZATION OF IMMERSED POROUS SOLIDS BASED ON THE CAPILLARY PHASE-SEPARATION CONCEPT

5.1 Introduction

Pore characteristics as well as the physico-chemical natures of porous solids play an important roll in many fields such as physisorption, chemisorption, membrane and catalysis. The increasing demands for these techniques and recent advance in production technology for porous material have been yielding various types of porous solids. Among them, as seen in macroreticular adsorbents, some porous materials will swell or shrink when immersed in a solvent in use. The swollen or shrunk state itself is the important characteristic for these kinds of solids. However, conventional methods for pore characterization such as physisorption of gas and mercury intrusion need evacuation before the measurements, which yield only 'dried' states of information.

It has been already shown in the preceding chapter that a similar phenomenon to the capillary condensation can occur in liquid phase if the interface of liquid-liquid equilibrium has curvature within narrow pore, and that the liquid phase adsorption isotherms of solutes with limited solubilities can be interpreted on the basis of this concept, Capillary Phase-Separation (CPS). The understanding for total amount adsorbed is quite similar to that of the mesopore analysis by physisorption. Hence the CPS phenomenon is tightly connected with the pore characteristics of solids immersed in a solvent.

Thus, we could estimate pore characteristics of immersed solids if we have a quantitative knowledge of the amount of surface adsorption in liquid phase onto non-porous solids.

As a simple test for this method, non-swelling porous solids in water were employed in this work. The pore size distributions (PSD) of the solids were estimated from liquid phase adsorption isotherms based on the CPS concept with the information of the amount adsorbed on non-porous solids of similar chemical composition, and compared with those calculated from nitrogen adsorption isotherms. The two distributions, namely, one obtained from adsorption of nitrobenzene from aqueous solution and the other from nitrogen adsorption were in sufficiently good agreement to show the potential power of the method proposed. The influence of the magnitude of surface adsorption, which may first bring uncertainty into the method, is further discussed.

5.2 Capillary phase-separation concept

The capillary phase-separation is a similar phenomenon to capillary condensation from thermodynamic aspect: a hindered liquid-liquid equilibrium could stand within a pore because of the presence of a curved interface of the two liquid phases. In other words, a solute-rich phase could be equilibrium with a solvent-rich phase at a lower concentration than the saturated. As shown in the previous chapter, the liquid-liquid equilibrium with curved interface is expressed by Eq.(4.13). As an approximation, Eq.(4.14) can be used for systems with small solubility, e.g., aqueous solutions of aromatic or aliphatic compounds.

5.3 Estimation of pore size distribution of immersed solids

The solute-rich phase of the hindered liquid-liquid equilibrium within a pore would be counted as adsorbed amount at a lower concentration than the saturated. Accordingly, the total amount adsorbed consists of two modes of *adsorption*, namely, the adsorption which arises from physico-chemical nature of the adsorbent surface, and the apparent amount by CPS which arises from the pore characteristics of the adsorbent especially in the mesopore range. This concept is quite the same as that employed in pore analysis of mesoporous solids by physisorption of gas. Then, the interrelation between liquid-phase adsorption isotherm and PSD of an immersed solid can now be understood in the same manner as that between gas-phase adsorption isotherm and PSD. Hence, with quantitative comprehension of CPS, PSD of immersed solid could be calculated from a liquid phase adsorption isotherm, and vice versa, if we have a knowledge of the adsorption on surface in liquid phase.

For the verification of the method, non-swelling mesoporous solids were used in this work. The PSD's of a solid were calculated both from nitrogen adsorption isotherm and from adsorption isotherm of an aromatic compound from aqueous solution, and compared.

The calculation scheme of PSD for immersed solids from liquid phase adsorption isotherm was similar to that of Dollimore and Heal (1964), which is for nitrogen isotherm and was also used here for calculation of PSD from nitrogen isotherm for comparison. Note that the present estimation method for immersed solids does not limit itself into this calculation procedure. Rather, any calculation scheme which is originally proposed for gas physisorption could be applied if its basis is the understanding of the total amount adsorbed as the sum of adsorption on surface and capillary

condensate, since the substitution of CPS for the latter adsorption mechanism would make the method applicable to immersed solids.

The adsorption on surface in liquid phase was expressed by a similar equation to that of the method for gas phase. Namely, it was expressed as "the statistical thickness" of the adsorption in liquid phase and assumed to follow Frenkel-type formula as shown by Eq.(4.15).

By this assumption, we have only one unknown parameter, t_o in Eq.(4.15) for the calculation of PSD of an immersed solid from a liquid-phase adsorption isotherm. The unknown parameter, t_o , is considered to be unique for combination of solute, solvent and solid. An aromatic compound in water was used as a solution in the present study. The parameter for carbonaceous solid was determined by using graphite as a nonporous solid, while a value determined in Chapter 4 was used for macroreticular adsorbents.

Because of relatively large experimental error for the measurement of liquid phase adsorption, a direct use of the liquid phase adsorption data would result in unrealistically oscillated pore distribution. Hence the data were smoothed by a cubic polynomial and the calculation for liquid phase was based on this function.

The procedure of the pore analysis is briefly explained below. The CPS phase can be approximated as a pure phase of adsorbate in this calculation because of the small solubility of water into the β-phase. Then the amount adsorbed by CPS can be converted to corresponding volume using density of pure liquid. The critical pore radius r_p corresponding to a concentration of an isotherm datum is calculated with r by Eq. (4.13) and t by Eq. (4.15).

Table 5.1 Physical properties of nitrobenzene

Molecular weight	[kg/mol]	0.123
Liquid density	[kg/m^3]	1.19 x10^3
Interfacial tension with water	[N/m]	25.7 x10^{-3}
Saturated concentration	[mol%]	0.0320

$$r_p = r + t \tag{5-1}$$

At any data point of the isotherm, the pores with smaller radii than the critical one corresponding to its concentration are supposed to be filled with the adsorbate while those with larger radii have the surface adsorption expressed by Eq. (4.15) and the solution with the concentration, which would have almost no contribution to the amount adsorbed. The difference in volume of amount adsorbed between adjacent data, ΔV , then, consists of volume of CPS in this pore range ΔV_c and the change in surface adsorption ΔV_s .

$$\Delta V = \Delta V_c + \Delta V_s \tag{5-2}$$

The latter is calculated using Eq.(4.15) together with the information of elemental surface areas of larger pores determined stepwise. Then ΔV_c and the corresponding pore volume in this pore range ΔV_p is determined. The calculation proceeds until the concentration becomes small enough so that the CPS phase does not contribute to the amount adsorbed.

5.4 Experimental

Adsorption isotherms of nitrobenzene from aqueous solution onto porous adsorbents were measured by a conventional batch adsorption method at 308

Table 5.2 Physical properties of adsorbents

Adsorbent	Nitrogen surface area $[m^2/g]$	Pore volume $[cm^3/g]$
EC	670	0.72
SP900	580	0.84
Graphite	9.9	-

K. The physical properties of the adsorbate are summarized in Table 5.1. The reagent of research grade provided by Wako Pure Chemicals Inc. was used with no further purification. The adsorbents are summarized in Table 5.2. EC, electric conductive porous carbonblacks, and SP900, whose chemical structure is of stylene-divinylbenzene block co-polymer, are typical mesoporous solids. The CPS would show a large contribution for these adsorbents. In addition to porous adsorbents of different origin, a non-porous solid was employed to examine the validity of using Eq.(4.15) for the statistical thickness of the adsorption in liquid phase. Before experimental usage, the carbonaceous adsorbents were washed with distilled water and evacuated at 383 K for 24 hours while the macroreticular adsorbents were washed first with methanol before done with distilled water, and then evacuated at 333 K for 48 hours.

The measurements were made by a conventional batch adsorption method. The adsorbent was added to 300 ml solution in an Erlenmeyer flask stopped by teflon-sealed screw cap to prevent the solute from evaporative loss. The flask was shaken in a thermostatted bath for 7 days. The equilibrium concentration was determined by an ultraviolet spectrophotometer (Shimadzu UV-260).

Nitrogen adsorption isotherms at 78 K were measured by the constant volume method to obtain the pore size distributions for comparison.

The nitrogen isotherms for the porous solids more or less showed hysteresis. The question, which branch to use for pore analysis, has been under discussion for many years. The PSD calculation in this study was based on the *adsorption* branches of isotherms for the purpose of comparison of gas phase and liquid phase: the liquid phase adsorption isotherms are considered to be close to the *adsorption* branches under the experimental condition of this study. An isotherm obtained by "batch" adsorption may sound closer to desorption branch since the initial concentration is higher than the equilibrium one. However, it should depend on the mass transfer mechanisms. The batch adsorption method might give partial characteristics of desorption branch if the external mass transfer resistance is small since the outermost portion of adsorbent particle would be exposed to a solution with higher concentration than the equilibrium one. On the other hand, the higher concentration might not be able to touch to the particle surface if the external mass transfer resistance is large, which might be the case in this study because no intensive mixing was made during the course of adsorption and because an acceleration of intraparticle mass transfer by so-called surface diffusion would be possible in the systems examined.

5.5 Results and discussion

5.5.1 Adsorption on non-porous solid from solution

The validity of using Eq.(4.15) as an expression for the adsorption on surface in liquid phase was tested with non-porous solid as shown in the section 4.5.3. The result showed fairly good agreement in most part of the concentration. In lower concentration range Eq.(4.15) overestimated the amount adsorbed. However, similarly to the case of isotherm estimation in Chapter 4, the estimation of porosity needs the amount adsorbed in middle or

higher range of the relative concentration. This characteristic of the present method would make the influence of the overestimate quite small again. As a whole, the utilization of the Frenkel formula for the adsorption on surface is thought to be appropriate for the capillarity estimation by the present method.

This t_0 value was used in the calculation of PSD for EC while it was 0.59 nm for macroreticular adsorbents, which was obtained in Chapter 4. Namely, the parameter t_0 was determined as shown in Table 4.3 for various combinations of adsorbent and adsorbate, which were obtained not by direct measurements on nonporous solids but by fitting experimental and calculated adsorption isotherms from solution on porous adsorbents using a method for isotherm estimation based on the CPS concept. As seen, the variation of the value is quite small for an adsorbate, nitrobenzene, over the adsorbents examined, while it shows relatively large variation over four kinds of adsorbates.

The insensitivity of the t_0 value to the adsorbents examined could be interpreted as follows. In the concentration range considered here the apparent coverage exceeds unity, which implies more opportunity for an adsorbed molecule to interact with other adsorbed molecules. This situation for the molecule reduces the importance of the interaction with the solid surface or with solvent molecules. As a result, the influence of the adsorbent-adsorbate interaction on the t_0 value becomes less important and the adsorbate-adsorbate interaction principally determines the t_0.

5.5.2 Comparison of calculated pore size distribution

The adsorption isotherm from aqueous solution on EC is shown in Figure 5.1. The solid line expresses the smoothed curve by the polynomial function. The smoothed curve is surely able to express the sigmoidal change of liquid phase adsorption in this system.

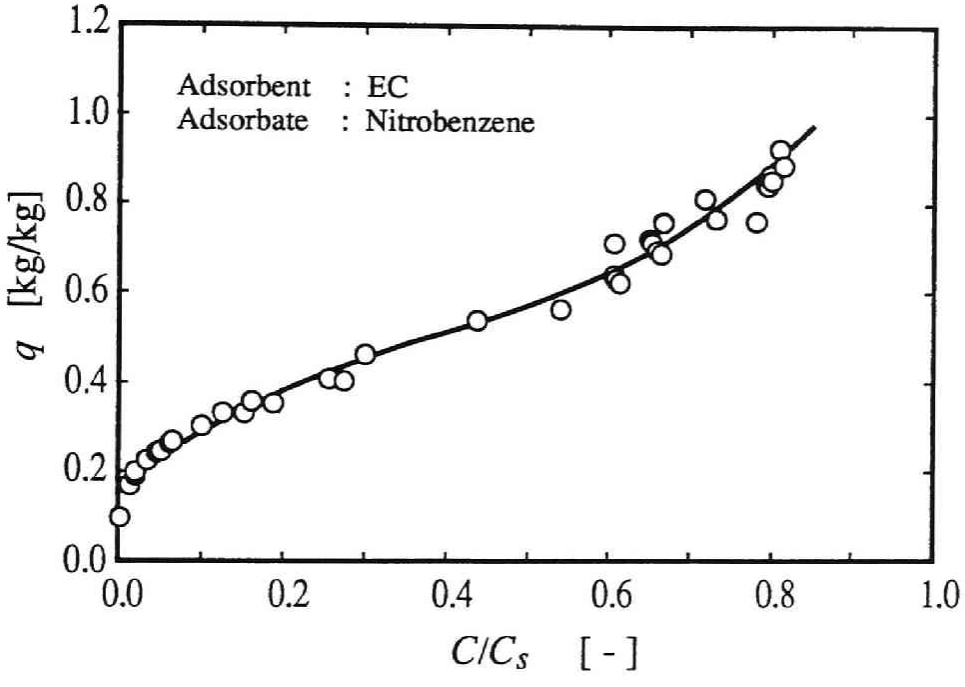

Figure 5.1. Liquid phase adsorption isotherm of nitrobenzene on EC

Figure 5.2 compares the PSD calculated from the isotherm in liquid phase shown in Figure 5.1 by the present method and the one from nitrogen adsorption at 78 K. The distribution from liquid phase has quite a similar form to that from physisorption of gas. Both qualitatively and quantitatively, the agreement is satisfactory in view of the usage of mesopore analysis presently applied. The agreement manifests the validity of the quantitative expression of the CPS, Eq.(4.14) and the calculation scheme of the present method for immersed solids.

Similar results are obtained as shown in Figures 5.3 and 5.4 for the macroreticular adsorbent SP900. In this case, the adsorbent has a rather clear peak in the distribution around 7 nm as shown by the gas phase result. The trial of mesopore analysis of immersed solid succeeded to find out this characteristic of the solid to yield fairly good agreement between the two distribution curves. As a whole, the present method has a potential power of detecting mesopore characteristics of solids in immersed state which could be applicable to swelling/shrinking solids in solvents.

5.5.3 Influence of surface adsorption parameter

The method needs information of surface adsorption in principle. The amount should be obtained by experiments on a nonporous solid with the same chemical composition as that of the porous solid to be examined. However, this kind of experiment often brings great difficulties because, in addition to generally arising difficulties in liquid phase adsorption, nonporous solids have quite small surface areas in general which result in hard-to-detect amounts adsorbed. Thus the measured surface adsorption may inevitably include large uncertainty. If we have a solute with small surface adsorption compared with the contribution by the CPS phase, the uncertainty

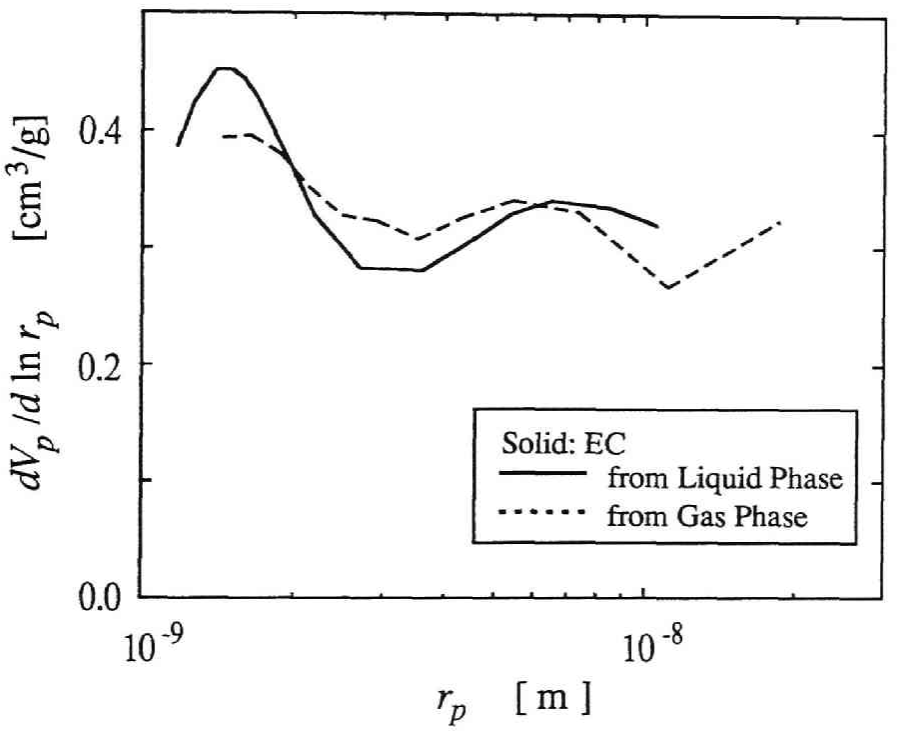

Figure 5.2. Comparison of PSD of EC from liquid phase and gas phase

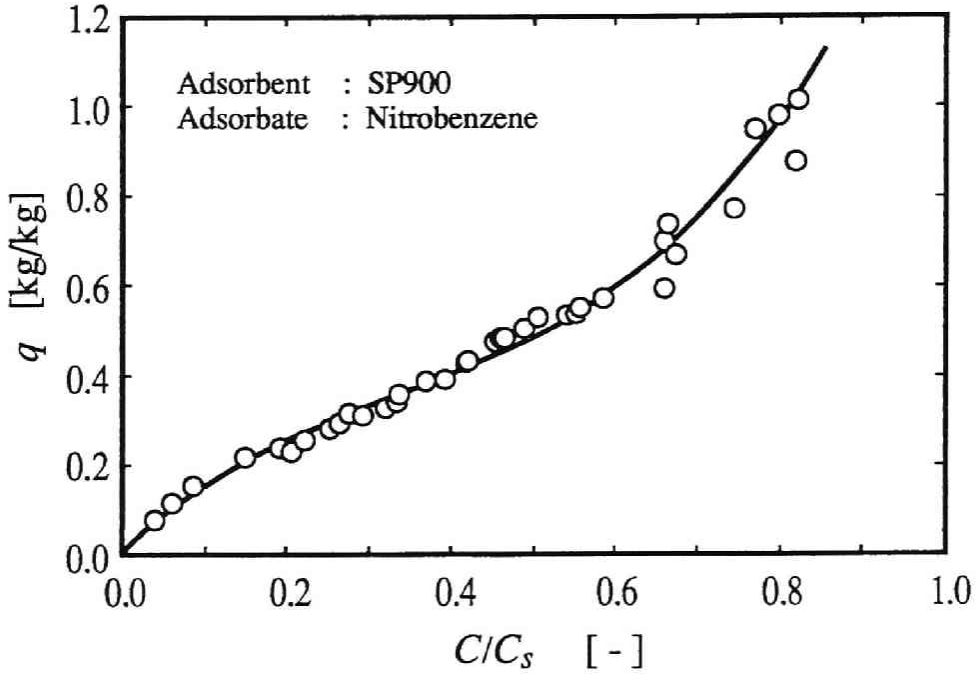

Figure 5.3. Liquid phase adsorption isotherm of nitrobenzene on SP900

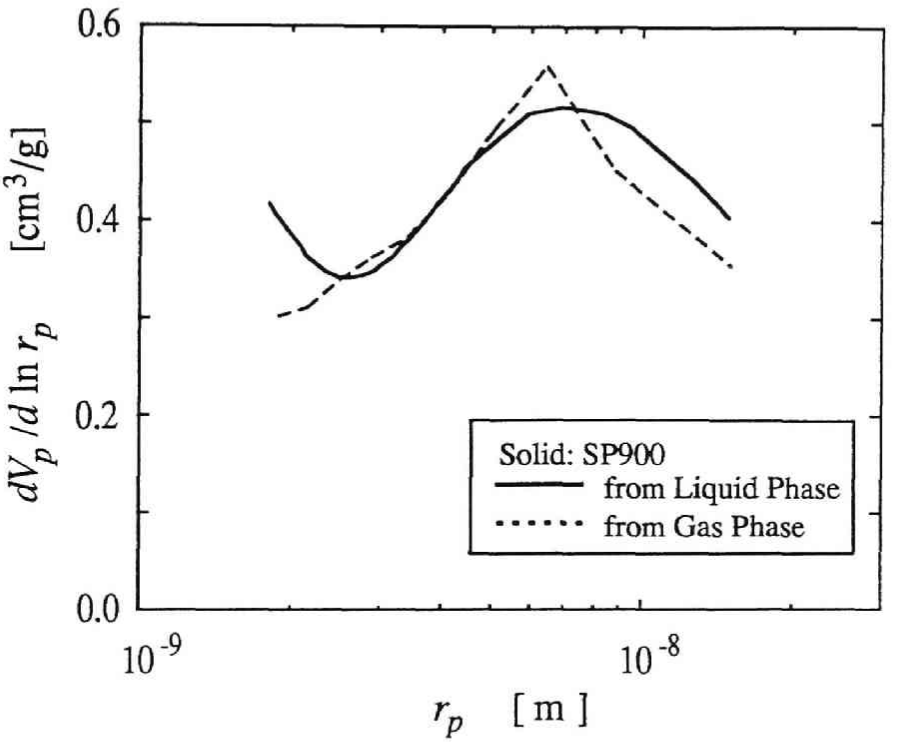

Figure 5.4. Comparison of PSD of SP900 from liquid phase and gas phase

involved in calculated PSD is expected to be reduced. By a simulative calculation, the nature of surface adsorption, or parametric sensitivity of t_o to calculated PSD's is considered as follows.

On the basis of the pore size distribution of SP900, two fictitious solutes were considered. One was with t_o of 0.6 nm, which was close to that of nitrobenzene, and the other with t_o of 0.1 nm, which was a model solute with small surface adsorption. With respective value of the parameter, fictitious liquid-phase adsorption isotherm for each solute was calculated from the PSD, the procedure of which was the reverse calculation of PSD determination. These isotherms were analyzed with different t_o values which included ± 50 % error from the original one as an example of the uncertainty of the parameter. Thus obtained PSD's with erroneous t_o were compared with the original one.

The *disturbed* PSD's are shown in Figures 5.5 and 5.6 together with the *true* PSD's. As seen, the overall feature of the distribution does not change significantly even with as much as 50% error in the surface adsorption parameter. Thus the present method has a desirable feature, not too sensitive to a parameter with large uncertainty. Further observation of the results clarifies the superiority of the solute with smaller surface adsorption. The peak height and location of the solute with smaller t_o are almost identical with the original ones while the other shows higher peak at greater pore radius with +50% error. The disturbance evoked by the error in the parameter is a cumulative one so that the difference will be bigger for solids with smaller pore radius while it will be smaller for solids with larger pore radius, which was confirmed in other simulative calculations made on different model solids though the results are not shown graphically here.

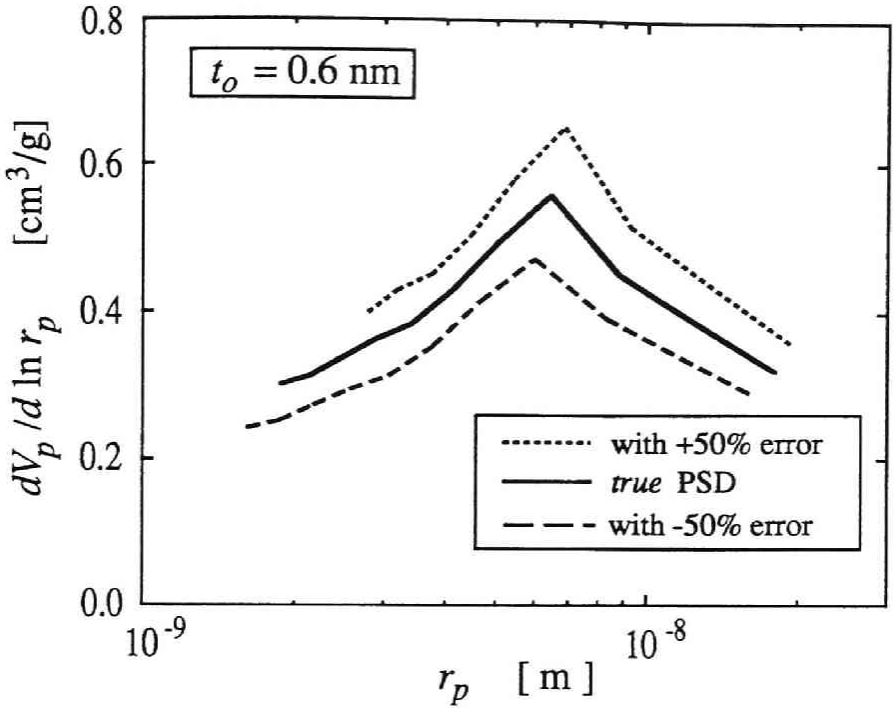

Figure 5.5. Disturbance in pore size distribution by error in the parameter; to =0.6 nm

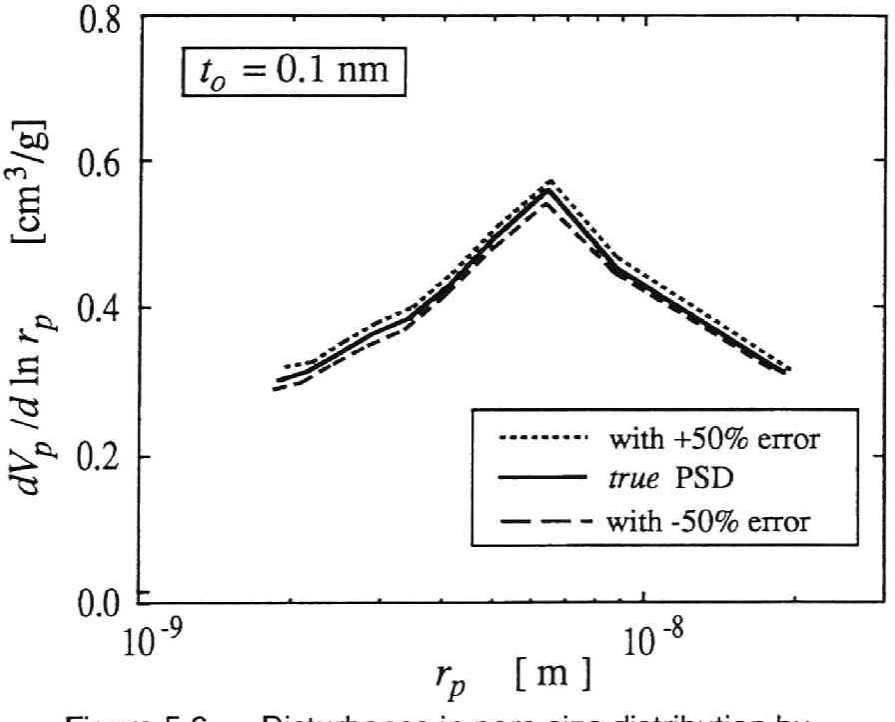

Figure 5.6. Disturbance in pore size distribution by error in the parameter; to =0.1 nm

Considering the characteristics of the surface adsorption parameter, a solute with smaller surface adsorption is desirable for the present method. It is especially appropriate to a solid with smaller pores, for which a larger surface adsorption parameter yields greater sensitivity to the error in the PSD. On seeking a suitable probe molecule for characterization of an immersed porous solid, the selection should be made on the strategy described above.

The relatively small sensitivity of calculated PSD on the surface adsorption parameter would suggest a complete neglect of surface adsorption itself in the calculation. For pore analysis by nitrogen adsorption, Brunauer *et al.* (1967) suggested the possibility of the neglect, together with the so-called modelless method, and found no significant change caused by the neglect. It might similarly apply to the present method. By the neglect, the obtained radius would be the "core" radius which does not include the thickness of the surface adsorption and hence is not exactly the pore characteristics. However, such information sometimes may be important in many practical applications, for example, comparison among porous solids with similar base material as seen in materials development. In those cases, one need not count for the surface adsorption, which greatly reduces the experimental efforts for the determination of pore size distribution.

5.6 Conclusions

A method for estimation of pore size distribution of solids immersed in solvents was proposed, which had its basis on the capillary phase-separation concept, or a hindered liquid-liquid equilibrium in narrow pore with curved interface. The method should be effective for determination of swollen or shrunk states of porous solids in solvents. The method was able to elucidate the pore characteristics of immersed solids from liquid phase adsorption

isotherms, which was confirmed by comparing the pore size distribution from liquid phase and that from nitrogen adsorption on non-swelling solids. The error in the surface adsorption parameter, which may be with relatively large uncertainty, was found to bring no significant disturbance into the distribution. This desirable nature of the parameter intensified itself with smaller surface adsorption amount.

CHAPTER 6

CONCLUSIONS AND REMARKS ON FURTHER STUDY

This thesis was dedicated to pursue deeper understanding of liquid-phase adsorption in two aspects of the intraparticle mass transfer and the equilibrium, aiming at findings with broader applicability with its clear limits. Through the experimental and theoretical study, the following conclusions were obtained.

The intraparticle mass transfer was studied in terms of surface diffusivity for adsorption of aromatic compounds from aqueous solution onto activated carbon. The concentration dependency in its strict meaning was measured in batch kinetic experiments with limited ranges of amount adsorbed. Equilibrium character of the adsorption systems studied was proved to follow the potential theory of adsorption. Consideration of elemental processes of surface diffusion clarified the importance of one of the elemental processes; the hole-making step within adsorbed phase for the movement of adsorbed molecules, to which few researchers have paid attention so far. The concentration dependency, along with its temperature dependency, was thus analyzed theoretically on the basis of Eyring's rate theory to yield a correlation equation for this dependence. In addition to its good performance on the correlation of the surface diffusivities measured in this study, the equation was proved to be a general form which includes some correlation equations proposed so far by other researchers, and was shown to have good accords with some previous works. Though the equation has two parameters which should be determined experimentally, rough estimates could be

possible because of their physical meanings defined clearly. These advantages of the present correlation could not be attained until the mechanism of surface diffusion was discussed in detail. The present model could provide not only the quantitative estimates but also, of course, a qualitative perspectives for mass transfer property of a given system.

Equilibrium characteristic of adsorption from dilute solution was considered on the basis of capillarity of adsorbent. The main idea was the possibility of a "capillary condensation" in liquid phase; a solute in solvent could be separated out as a liquid into small pores by capillary effect similar to the capillary condensation. The "liquid-phase capillary condensation" is termed as Capillary Phase-Separation (CPS). A thermodynamic analysis of liquid-liquid equilibrium with curved interface gave an equation for the relation between the concentration reduction in bulk phase and the curvature of the interface, or the pore radius. This equation had a complicated formula, comparing with the Kelvin equation, because of the increased number of components in liquid phase, but reduced to a similar form to the Kelvin equation if solubility was small. The isotherms measured on variety of combination of solutes and mesoporous solids clearly manifested the indispensable contribution of the CPS, adding to adsorption on surface. The concept was utilized as a scheme for isotherm estimation, the applicability of which was proved for many systems with liquid-liquid equilibrium and was denied for solute with liquid-solid equilibrium. Based on this understanding of the adsorption mechanism, one may be able to know a suitable pore size for adsorption of a given solute. Thus, the understanding of equilibrium attained in this work could stand as a guideline for pore size in liquid phase adsorption.

Another utilization of the CPS concept could be pore size detection of porous solids immersed in liquid, which should be of much importance for solids

with swelling or shrinking nature. The possibility of the *in situ* characterization was demonstrated on model porous solids of hard structure for the verification. Many difficulties, such as the search for solutes with large contribution of CPS, possible error brought by surface adsorption and relatively large experimental efforts, could lie before application to a swelling/shrinking solid with unknown surface character. These difficulties, however, should be worth challenging if the transformed state itself is the indispensable information on a given porous solid.

The combination of the CPS concept with intraparticle mass transfer would give a possibility of anomalously large transport rate within porous media; the CPS phase might be driven, not by a concentration gradient but, by the gradient of capillary suction pressure similarly to the phenomena in gas-phase adsorption with capillary condensation as shown by Tamon *et al.* (1981). Experiments were made on this subject by the author and co-workers for adsorption of aromatics from aqueous solution onto mesoporous solids of macroreticular adsorbents though the results are not stated in this thesis. An incipient great increase of mass transfer rate was detected in higher range of relative concentration. To the author's regret, however, the accuracy of the data was not sufficient to prove the definite existence of the phenomenon. If such large transfer rate could be possible, an effective membrane separation, for example, could be possible in such system with CPS. Again, note that the higher relative concentration could be still dilute if solubility is small. The author wishes to pursue the subject aiming at the application to separation technique.

A more precise analysis could give a detection of new phenomena and should be of much importance to an advance in the academic aspect. A more precise analysis, on the other hand, might bring the necessity of increased

information, or physical properties, to be determined experimentally for the design of industrial processes. To pursue a sophisticated and effective way of data acquisition and computational design, a precise analysis of a phenomenon should be accompanied by a deeper understanding of the phenomenon which could give broader sight and applicability limits. Also to be elucidated is essential functional relation into which all necessary properties and characteristics for design of a given system are concentrated. These two aspects of information, deeper understanding and essential functional relation would help each other and could strengthen their power as a technology. The reason the potential theory of adsorption still has much importance might come from this feature. Adsorption onto porous solids depends both on the physico-chemical nature of solid surface and on pore characteristics of solid. Adsorption phenomena are often analyzed in these two aspects. The potential theory, however, does never separate them. Instead, it simply gives a "Characteristic Curve" which interconnects the potential and adsorption volume regardless of the contribution of surface or that of pores. Of course, the deepened understanding of physisorption has been adding the background of the theory with which one could speculate applicability for a given system. It might be more than often that the approach using the potential theory is a powerful tool for adsorption processes.

The author has much been stimulated by this simple beauty of the potential theory since starting the research on adsorption. He deeply desires to find out a "characteristic function" for adsorption kinetics and that for adsorbent-adsorbate interactions. The work should not limit itself in adsorption technique but shall broaden out to the large field of separation engineering. Now, he has started his walk from a milestone of this dissertation toward the goal.

NOMENCLATURE

A_p	=	particle surface area	[m^2]
a	=	coefficient of linear expression of ΔE_a with q_{st} in Chapter 2	[-]
a	=	ratio of activation free energy to energy of making a hole of volume per molecule in Chapter 3	[-]
a_i	=	activity of i-component	[-]
Bi	=	Biot number	[-]
C	=	concentration of adsorbate	[kg/m^3]
C_i	=	initial concentration	[kg/m^3]
C_s	=	saturated concentration of adsorbate	[kg/m^3]
D_{ab}	=	molecular diffusivity	[m^2/s]
D_C	=	effective diffusivity defined by Eq.(3.17)	[m^2/s]
D_e	=	effective diffusivity	[m^2/s]
D_p	=	pore diffusivity	[m^2/s]
D_S	=	surface diffusivity	[m^2/s]
D_S^*	=	surface diffusivity at $q = q^*$	[m^2/s]
ΔE_a	=	activation energy for mobility	[J/mol]
ΔE_{vap}	=	evaporative energy	[J/mol]
F	=	force acting on adsorbed molecules	[N]
ΔF_{ads}	=	adsorption potential	[J/mol]
$\Delta F^{\ddagger}$	=	activation free energy of surface diffusion	[J/mol]
g_n	=	roots of Eq.(2.10)	[-]
ΔH_{sol}	=	heat of dissolution	[J/mol]
ΔH_{vap}	=	heat of vaporization	[J/mol]
h	=	Planck's constant	[J·s]
J_p	=	mass flux by pore diffusion	[$kg/(m^2 \cdot s)$]

J_S	=	mass flux by surface diffusion	[kg/(m^2•s)]
J_t	=	total mass flux	[kg/(m^2•s)]
K	=	dq/dC ; slope of adsorption isotherm	[m^3/kg]
k	=	external mass transfer coefficient in Chapter 2	[m/s]
k	=	rate constant of surface diffusion in Chapter 3	[1/s]
k_B	=	Boltzmann's constant	[J/K]
k_o	=	pre-exponential factor for mobility	[m/(N•s)]
L	=	volume of solution in batch experiment	[m^3]
N_A	=	Avogadro's number	[1/mol]
n	=	reciprocal exponent of Freundlich isotherm	[-]
P	=	pressure	[Pa]
P'	=	pressure in separation phase	[Pa]
P_o	=	standard pressure	[Pa]
q	=	amount adsorbed	[kg/kg]
q^*	=	standard amount adsorbed in Eq.(2.17)	[kg/kg]
q_{st}	=	isosteric heat of adsorption	[J/mol]
R	=	gas constant	[J/(mol•K]
R_p	=	radius of adsorbent particle	[m]
r	=	radial coordinate	[m]
r_p	=	pore radius	[m]
T	=	temperature	[K]
T_b	=	boiling temperature	[K]
t	=	time in Chapter 2	[s]
t	=	statistical thickness of adsorption in Chapter 4 and 5	[m]
t_o	=	parameter for statistical thickness of adsorption in liquid phase	[m]
u_a	=	mobility of adsorbed molecules	[m/(N•s)]
u_{ao}	=	constant defined by Eq.(2.26)	[m/(N•s)]
u_{ao}^*	=	constant defined by Eq.(3.12)	[m/(N•s)]
V	=	amount adsorbed expressed in liquid volume	[m^3/kg]
V_b	=	volume of bulk liquid	[m^3]

V_p	=	pore volume	[m^3/kg]
V_{sat}	=	adsorption volume at saturation	[m^3/kg]
ΔV	=	difference in adsorption volume	[m^3/kg]
ΔV_c	=	difference in adsorption volume by CPS	[m^3/kg]
ΔV_s	=	difference by surface adsorption	[m^3/kg]
v	=	molar volume	[m^3/mol]
v_a	=	average velocity of adsorbed molecules	[m/s]
W	=	adsorption volume	[m^3/kg]
W_a	=	adsorbent dosage	[kg]
X	=	mole fraction	[-]
z	=	distance coordinate (along the macroscopic direction of diffusion)	[m]

Greek Letters

α	=	constant given by Eq.(2.12)	[-]
ε	=	porosity of adsorbent	[-]
λ	=	distance between neighboring equilibrium positions	[m]
μ	=	tortuosity factor in Chapter 2	[-]
μ	=	chemical potential in Chapter 4 and 5	[J/mol]
μ_a	=	chemical potential in adsorbed state	[J/mol]
μ_l	=	chemical potential in solution	[J/mol]
μ_s	=	tortuosity factor for surface diffusion	[-]
θ	=	contact angle	[rad]
ρ_{app}	=	apparent density of adsorbent	[kg/m^3]
σ	=	interfacial tension	[N/m]
τ	=	dimensionless time	[-]

Subscripts

A	=	component A
B	=	component B

b = bulk liquid

bo = initial condition of bulk liquid

o = pertaining to point A in Figure 2.1

S = normal equilibrium

∞ = pertaining to point C in Figure 2.1

Superscripts

α = solvent-rich phase

β = solute-rich phase

$^{\circ}$ = pure state

* = infinite dilution

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